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TITLE

OLEFIN POLYMER AND PROCESS FOR PREPARING THE SAME

Ins AI TECHNICAL FIELD

- 5 The present invention relates to olefin polymers and processes for preparing the same. More particularly, the invention relates to an olefin polymer having an extremely narrow molecular weight distribution, an olefin polymer containing two kinds of specific polymer blocks,
- 10 the above-mentioned olefin polymers having a functional group at the terminal, a block copolymer, and processes for preparing these olefin polymers.

BACKGROUND ART

- 15 Polymers having narrow molecular weight distribution and specific molecular weight, polymers having a functional group introduced at the terminal and block polymers having different segments bonded to each other exhibit various useful properties, so that they are very
- 20 important from not only the academic viewpoint but also the industrial viewpoint.

It is generally well known that in the production of polymers having such specific structures, living polymerization wherein neither termination reaction nor

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chain transfer reaction substantially takes place during the polymerization is effective.

However, if the polymerization is carried out under usual conditions using a Ziegler catalyst or a  
5 metallocene catalyst that is generally used as an olefin polymerization catalyst to produce polymers having the above specific structures, chain transfer reactions of the growing polymer chains frequently take place, and it is very difficult to produce olefin polymers by living  
10 polymerization. For example, it has been made clear by analyses of molecular weight distribution, composition distribution, etc. that when a block copolymer is intended to be synthesized using a known catalyst system, a mixture of homopolymer and random copolymer is produced  
15 (Boor, "Ziegler-Natta Catalyst and Polymerization", Academic Press Co., 1979).

Under such circumstances, some researches of living polymerization of olefins have been reported.

For example, living polymerization of propylene  
20 using a specific vanadium catalyst has been reported by Doi, et al. (Macromolecules, vol. 19, p. 2896, 1986). In this process, however, an extremely low polymerization temperature such as a temperature of  $-78^{\circ}\text{C}$  to  $-40^{\circ}\text{C}$  is necessary, and the polymerization activity is several  
25 tens g-polymer/mmol-M·h and is not commercially

10 Brookhart, et al. and McConvill, et al. have reported living polymerization of higher  $\alpha$ -olefins such as propylene and 1-hexene with specific nickel complex or titanium complex (Journal of American Chemical Society, vol. 118, p. 11664, 1996, Journal of American Chemical  
15 Society, vol. 118, p. 10008, 1996). Also in this process, low-temperature polymerization at a temperature of not higher than 0°C is necessary in many cases, and the resulting polymer has an atactic structure having no stereoregularity. Moreover, it is difficult to produce  
20 polyethylene or an ethylene polymer by living polymerization using the nickel complex or the titanium complex.

Soga, Shiono, et al. have studied living polymerization of propylene using a metallocene catalyst, but in this process, an extremely low temperature such as

a temperature of  $-78^{\circ}\text{C}$  to  $-60^{\circ}\text{C}$  is necessary, and the levels of polymerization activity and molecular weight of the resulting polymer are low (Macromolecule, vol. 31, p. 3184, 1998, Macromolecule Rapid Communication, vol. 20, p. 637, 1999).

As a synthesis of polyethylene by living polymerization, that is generally said be difficult, Nakamura, et al. have reported a process of using a niobium or tantalum complex, and Yasuda, et al. have reported a process of using a samarium complex. In these processes, however, there are defects that the activity is low, the molecular weight of the resulting polyethylene is limited to about 100,000, and copolymerization of comonomers other than ethylene is infeasible (Journal of American Chemical Society, vol. 115, p. 10990, 1993).

As a synthesis of a block polymer having different segments bonded to each other, a process of using a specific metallocene catalyst has been reported (International Patent Publication WO91/12285, WO94/21700). In this process, however, the activity is low, and low-temperature polymerization ( $-10^{\circ}\text{C}$  to  $0^{\circ}\text{C}$ ) is essential. Moreover, it is described that the blocking efficiency is decreased to less than 10 % by increasing the polymerization temperature to  $10^{\circ}\text{C}$ . On this account,



production of a block copolymer at an industrially usually used polymerization temperature (50°C to 75°C) is impossible. Also in case of low-temperature polymerization, the molecular weight distribution ( $M_w/M_n$ ), that is an indication of living polymerizability, of the block copolymer is not less than 1.35 and is not narrow, so that this polymerization is not living polymerization sufficiently controlled. Therefore, most of the products contain large amounts of non-block polymers as by-products, and fractionation to remove the unnecessary polymers is essential as a post treatment. Thus, there are many industrial restrictions.

Accordingly, development of a process wherein living polymerization of olefins can be carried out at an industrially available high temperature with high polymerization activity is of industrially very great value.

Under such circumstances, the present applicant has found, as novel olefin polymerization catalysts, transition metal compounds having a salicylaldehyde ligand, and has also found that when a transition metal compound having a specific structure selected from the transition metal compounds having a salicylaldehyde ligand is used, living polymerization proceeds at an industrially available high temperature with activity

extremely higher than that of hitherto known living polymerization, and production of polyolefins having high molecular weight and narrow molecular weight distribution and polyolefins or block copolymers having functional groups quantitatively introduced at the terminals is feasible. Based on the finding, the present invention has been accomplished. The present applicant has furthermore found a process for efficiently producing such polymers, and accomplished the present invention.

It is an object of the invention to provide olefin polymers exhibiting various useful properties, such as a polymer having a narrow molecular weight distribution and a specific molecular weight, a polymer having a functional group introduced at the terminal and a block polymer having different segments bonded to each other. It is another object of the invention to provide processes for preparing these olefin polymers. It is a further object of the invention to provide processes for efficiently preparing such polymers.

#### DISCLOSURE OF THE INVENTION

The olefin polymer according to the invention is a polymer of at least one olefin selected from olefins of 2 to 20 carbon atoms and has a number-average molecular weight of not less than 500 and Mw/Mn (Mw: weight-average

molecular weight, Mn: number-average molecular weight) of not more than 1.5. Such a polymer is sometimes referred to as a "monodisperse polyolefin" hereinafter.

The monodisperse polyolefin of the invention is, for  
5 example, polyethylene, high-density polyethylene  
(referred to as "HDPE" hereinafter), linear low-density  
polyethylene (referred to as "LLDPE" hereinafter),  
polybutene, a copolymer of ethylene and at least one  
olefin selected from olefins of 4 to 20 carbon atoms,  
10 dienes and cycloolefins, or a copolymer of propylene and  
at least one olefin selected from olefins of 4 to 20  
carbon atoms, dienes and cycloolefins.

The monodisperse polyolefin of the invention is, for  
example, a polymer of ethylene, which has a number-  
15 average molecular weight of not less than 110,000 and  
Mw/Mn of not more than 1.5, or a polymer of at least one  
olefin selected from olefins of 3 to 20 carbon atoms,  
which has a number-average molecular weight of not less  
than 500, Mn/Mn of not more than 1.5 and a melting point  
20 of not lower than 70°C.

The monodisperse polyolefin of the invention is, for  
example, an olefin polymer which is a polymer of  
propylene or butene and has a racemic diad (r), as  
measured by  $^{13}\text{C}$ -NMR, of not less than 0.85, or a polymer

which is an ethylene/propylene copolymer and has an ethylene content of not less than 60 % by mol.

The olefin polymer according to the invention is, for example, an olefin polymer which is an olefin  
5 copolymer of at least two olefins selected from olefins of 2 to 20 carbon atoms, has a number-average molecular weight of not less than 500 and is a tapered polymer containing a segment wherein composition of two or more monomers continuously changes in the polymer chain. A  
10 tapered polymer having Mw/Mn of not more than 2.5 and a tapered polymer having an ethylene content of not less than 30 % by mol are also available.

The olefin polymer according to the invention is, for example, an olefin copolymer which comprises a  
15 monomer unit  $M_1$  derived from an olefin of 2 to 20 carbon atoms and at least one monomer unit  $M_2$  that is different from the monomer unit  $M_1$ , and has the following properties:

$[M_1 \cdot M_2]$ ,  $[M_1 \cdot M_1]$ ,  $[M_2 \cdot M_2]$ ,  $[M_1]$  and  $[M_2]$ , as  
20 measured by  $^{13}\text{C}$ -NMR, satisfy the following relations:

$$1 > [M_1 \cdot M_2] / (2 \times [M_1] \times [M_2])$$

$$1 > [M_1 \cdot M_2]^2 / (4 \times [M_1 \cdot M_1] \times [M_2 \cdot M_2])$$

wherein  $[M_1]$  is a molar fraction of the monomer unit  $M_1$ ,  
 $[M_2]$  is a molar fraction of the monomer unit  $M_2$ ,  $[M_1 \cdot M_2]$   
25 is a molar fraction of a unit in which the monomer unit

M<sub>1</sub> and the monomer unit M<sub>2</sub> are adjacent to each other, [M<sub>1</sub>·M<sub>1</sub>] is a molar fraction of a unit in which the monomer unit M<sub>1</sub> and the monomer unit M<sub>1</sub> are adjacent to each other, and [M<sub>2</sub>·M<sub>2</sub>] is a molar fraction of a unit in which the monomer unit M<sub>2</sub> and the monomer unit M<sub>2</sub> are adjacent to each other.

The olefin polymer according to the invention is, for example, a polymer satisfying the above relations and having Mw/Mn of not more than 2.5, an olefin copolymer wherein an isolated monomer unit M<sub>1</sub> and a sequence of two or more continuous monomer units M<sub>1</sub> are both detected in the polymer chain by means of <sup>13</sup>C-NMR, or an olefin copolymer wherein a sequence of two continuous monomer units M<sub>1</sub> and a sequence of three or more continuous monomer units M<sub>1</sub> are both detected in the polymer chain by means of <sup>13</sup>C-NMR.

In the above polymers, the monomer unit M<sub>1</sub> is preferably an ethylene unit. An olefin copolymer wherein a sequence of two or more continuous methylene groups is detected by means of <sup>13</sup>C-NMR and a sequence of two continuous methylene groups and a sequence of three or more continuous methylene groups are both detected is also available.

Another embodiment of the olefin polymer of the invention is an olefin block copolymer comprising:

(i) a polymer block obtained from at least one olefin selected from olefins of 2 to 20 carbon atoms, and

- (ii) a polymer block that is obtained from at least one olefin selected from olefins of 2 to 20 carbon atoms and is different from the polymer block (i).
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The olefin block copolymer is, for example, a polymer comprising two or more polymer blocks, adjacent polymer blocks of which are different from each other, and having a number-average molecular weight of not less than 500 and Mw/Mn of not more than 2.5.

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The olefin block copolymer is, for example, an olefin polymer which is a diblock copolymer comprising two polymer blocks and has Mw/Mn of less than 1.35, an olefin polymer which is a triblock copolymer comprising three polymer blocks and has Mw/Mn of less than 1.80, or a polymer which is a multiblock copolymer comprising four or more polymer blocks and has Mw/Mn of less than 2.00.

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The above olefin block copolymer is, for example, a polymer wherein each polymer block is selected from polyethylene, HDPE, LLDPE, a copolymer of ethylene and at least one olefin selected from olefins of 3 to 20 carbon atoms, dienes and cycloolefins, atactic polypropylene (referred to as "ata-polypropylene" hereinafter), isotactic polypropylene (referred to as "iso-polypropylene" hereinafter), syndiotactic polypropylene

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(referred to as "syn-polypropylene" hereinafter), a copolymer of propylene and at least one olefin selected from olefins of 3 to 20 carbon atoms, dienes and cycloolefins, and the aforesaid tapered polymer.

- 5        Also available is a diblock copolymer or a triblock copolymer wherein each polymer block is selected from polyethylene, HDPE, LLDPE, an ethylene/propylene copolymer, an ethylene/butene copolymer, an ethylene/hexene copolymer, an ethylene/octene copolymer, 10        ata-polypropylene, syn-polypropylene, a propylene/butene copolymer and a propylene/hexene copolymer.

The polymer block (i) and the polymer block (ii) are each selected from, for example, the following polymer blocks (a), (b) and (c):

- 15        (a) a polymer block obtained from ethylene,  
         (b) a polymer block obtained from one  $\alpha$ -olefin selected from  $\alpha$ -olefins of 3 to 20 carbon atoms, and  
         (c) a polymer block obtained from two or more  $\alpha$ -olefins selected from  $\alpha$ -olefins of 2 to 20 carbon atoms.

- 20        The olefin block copolymer is, for example, a polymer containing at least one of the polymer block (a) which has a number-average molecular weight of 110,000 to 10,000,000 and Mw/Mn of not more than 1.5.

- 25        A further embodiment of the olefin polymer according to the invention is an olefin polymer having a functional

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5 comprises the monodisperse polyolefin, the tapered polymer, the olefin copolymer or the olefin block copolymer.

$$L_mMX_n$$

(I)



wherein M is a transition metal atom selected from Group 3 to Group 11 of the periodic table,

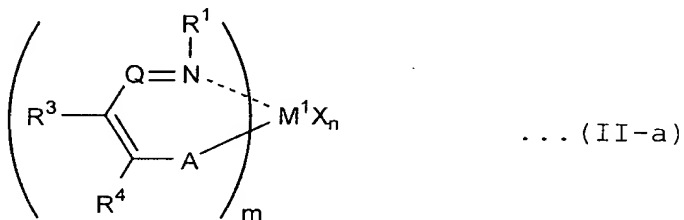
m is an integer of 1 to 5,

n is a number satisfying a valence of M,

- 5 L is a ligand coordinated to the central metal M and is a ligand having a heteroatom which has no direct bond to the central metal M, and

- X is an oxygen atom, a hydrogen atom, a halogen atom, a hydrocarbon group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a phosphorus-containing group, a halogen-containing group, a heterocyclic compound residue, a silicon-containing group, a germanium-containing group or a tin-containing group, and when n is 2 or greater, plural groups indicated by X may be the same or different, and plural groups indicated by X may be bonded to form a ring.
- 10
- 15

- The transition metal compound is, for example, a transition metal compound represented by the following formula (II-a) or (II-b);
- 20



wherein  $M^1$  is a transition metal atom selected from Group 3 to Group 11 of the periodic table,

m is an integer of 1 to 5,

- 5        Q is a nitrogen atom or a carbon atom having a substituent  $R^2$ ,

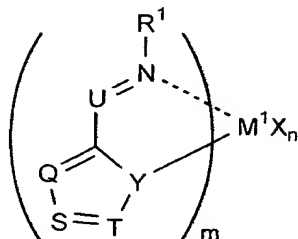
A is an oxygen atom, a sulfur atom, a selenium atom or a nitrogen atom having a substituent  $R^5$ ,

- 10        $R^1$  is a hydrocarbon group having one or more heteroatoms or a hydrocarbon group having one or more heteroatom-containing groups,

- 15        $R^2$  to  $R^5$  may be the same or different and are each a hydrocarbon group, a halogen atom, a hydrogen atom, a hydrocarbon-substituted silyl group, an oxygen-containing group, a nitrogen-containing group, a sulfur-containing group, a boron-containing group, an aluminum-containing group, a phosphorus-containing group, a halogen-containing group, a heterocyclic compound residue, a silicon-containing group, a germanium-containing group or  
20       a tin-containing group, two or more of  $R^2$  to  $R^5$  may be bonded to form a ring, and when m is 2 or greater,  $R^1$ s,  $R^2$ s,  $R^3$ s,  $R^4$ s and  $R^5$ s may be the same or different, and one group of  $R^2$  to  $R^5$  contained in one ligand and one group of  $R^2$  to  $R^5$  contained in other ligands may be  
25       bonded,

n is a number satisfying a valence of  $M^1$ , and  
 X has the same meaning as that of X in the aforesaid  
 formula (I);

5



... (II-b)

10 wherein  $M^1$  is a transition metal atom selected from Group  
 3 to Group 11 of the periodic table,

m is an integer of 1 to 5,

Y is a nitrogen atom or a phosphorus atom,

15 U is a carbon atom having a substituent  $R^6$ , a  
 nitrogen atom or a phosphorus atom,

Q is a carbon atom having a substituent  $R^7$ , a  
 nitrogen atom or a phosphorus atom,

S is a carbon atom having a substituent  $R^8$ , a  
 nitrogen atom or a phosphorus atom,

20 T is a carbon atom having a substituent  $R^9$ , a  
 nitrogen atom or a phosphorus atom,

$R^1$  and  $R^6$  to  $R^9$  are each the same atom or group as  
 described with respect to  $R^1$  and  $R^2$  to  $R^5$  in the formula  
 (II-a), and when m is 2 or greater,  $R^1$ s,  $R^6$ s,  $R^7$ s,  $R^8$ s

25 and  $R^9$ s may be the same or different, and one group of  $R^6$

to  $R^9$  contained in one ligand and one group of  $R^6$  to  $R^9$  contained in other ligands may be bonded,

$n$  is a number satisfying a valence of  $M^1$ , and

$X$  has the same meaning as that of  $X$  in the aforesaid

5 formula (I).

Similarly to the transition metal compound represented by the formula (I), the transition metal compound represented by the formula (II-a) or (II-b) preferably has properties that the distance between the  
10 heteroatom, which has no direct bond to the central metal  $M$  and is nearest to the central metal  $M$ , and hydrogen at the  $\beta$ -position is not more than 3.0 Å and the electrostatic energy is not more than 10 kJ/mol.

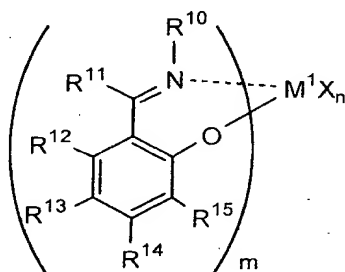
The transition metal compound represented by the  
15 formula (II-a) or (II-b) is preferably a compound wherein  $R^1$  is an aromatic hydrocarbon group, an aliphatic hydrocarbon group or an alicyclic hydrocarbon group, selected from a phenyl group having, at at least one position of the 2-position and the 6-position, when the  
20 position of the carbon atom bonded to nitrogen is the 1-position, one or more substituents selected from a heteroatom and a heteroatom-containing group, or has, at at least one position of the 3-position, the 4-position and the 5-position, at least one substituent selected  
25 from a heteroatom other than a fluorine atom, a fluorine-

containing group having one carbon atom and not more than two fluorine atoms, a fluorine-containing group having two or more carbon atoms, and a group containing a heteroatom other than a fluorine atom, and when R<sup>1</sup> is an aromatic hydrocarbon group other than a phenyl group, an aliphatic hydrocarbon group or an alicyclic hydrocarbon group, this group has at least one substituent selected from a heteroatom and a heteroatom-containing group.

In the transition metal compound represented by the formula (II-a) or (II-b), when the position of the carbon atom bonded to nitrogen is the 1-position, R<sup>1</sup> is preferably a halogen-containing hydrocarbon group of 1 to 30 carbon atoms selected from a phenyl group having, at at least one position of the 2-position and the 6-position, one or more substituents selected from a halogen atom and a halogen-containing group, a phenyl group having, at at least one position of the 3-position, the 4-position and the 5-position, at least one substituent selected from a fluorine-containing group having one carbon atom and not more than two fluorine atoms, a fluorine-containing group having two or more carbon atoms, a chlorine atom, a bromine atom, an iodine atom, a chlorine-containing group, a bromine-containing group and an iodine-containing group, an aromatic hydrocarbon group other than a phenyl group having at

least one substituent selected from a halogen atom and a halogen-containing group, an aliphatic hydrocarbon group having at least one substituent selected from a halogen atom and a halogen-containing group, and an alicyclic hydrocarbon group having at least one substituent selected from a halogen atom and a halogen-containing group.

The transition metal compound is, for example, a transition metal compound represented by the following formula (III):



... (III)

wherein  $M^1$  is a transition metal atom selected from Group 4 to Group 5 of the periodic table,

$m$  is 1 or 2,

$R^{10}$  is an aromatic hydrocarbon group, an aliphatic hydrocarbon group or an alicyclic hydrocarbon group, when  $R^1$  is a phenyl group and the position of the carbon atom bonded to nitrogen is the 1-position, this phenyl group has, at at least one position of the 2-position and the 6-position, one or more substituents selected from a

heteroatom and a heteroatom-containing group, or has, at at least one position of the 3-position, the 4-position and the 5-position, at least one substituent selected from a heteroatom other than a fluorine atom, a fluorine-containing group having one carbon atom and not more than two fluorine atoms, a fluorine-containing group having two or more carbon atoms, and a group containing a heteroatom other than a fluorine atom, and when R<sup>10</sup> is an aromatic hydrocarbon group other than a phenyl group, an aliphatic hydrocarbon group or an alicyclic group, this group has at least one substituent selected from a heteroatom and a heteroatom-containing group,

R<sup>11</sup> to R<sup>14</sup> may be the same or different and are each a hydrogen atom, a halogen atom, a halogen-containing group, a hydrocarbon group, a hydrocarbon-substituted silyl group, an oxygen-containing group, a nitrogen-containing group or a sulfur-containing group,

R<sup>15</sup> is a halogen atom, a halogen-containing group, a hydrocarbon group or a hydrocarbon-substituted silyl group,

n is a number satisfying a valence of M, and

X has the same meaning as that of X in the aforesaid formula (I).

In the transition metal compound represented by the formula (III), when the position of the carbon atom

bonded to nitrogen is the 1-position,  $R^{10}$  is preferably a halogen-containing hydrocarbon group of 1 to 30 carbon atoms selected from a phenyl group having, at at least one position of the 2-position and the 6-position, one or

5 more substituents selected from a halogen atom and a halogen-containing group, a phenyl group having, at at least one position of the 3-position, the 4-position and the 5-position, at least one substituent selected from a

10 fluorine-containing group having one carbon atom and not more than two fluorine atoms, a fluorine-containing group having two or more carbon atoms, a chlorine atom, a bromine atom, an iodine atom, a chlorine-containing group, a bromine-containing group and an iodine-containing group, an aromatic hydrocarbon group other than a phenyl group

15 having at least one substituent selected from a halogen atom and a halogen-containing group, an aliphatic hydrocarbon group having at least one substituent selected from a halogen atom and a halogen-containing group, and an alicyclic hydrocarbon group having at least

20 one substituent selected from a halogen atom and a halogen-containing group.

By the above process, for example, the monodisperse polyolefin, the tapered polymer or the olefin block copolymer can be prepared.

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presence of an olefin polymerization catalyst comprising the above-mentioned transition metal compound to prepare a polymer block,

- (2) a step of polymerizing at least one olefin  
5 selected from olefins of 2 to 20 carbon atoms in the presence of the polymer block prepared in the step (1) to prepare a polymer block which is different from the polymer block prepared in the step (1), and

- (3) a step of polymerizing at least one olefin  
10 selected from olefins of 2 to 20 carbon atoms in the presence of the polymer block prepared in the step (1) and the polymer block prepared in the step (2) to prepare a polymer block which is different from the polymer blocks prepared in the previous step.

- 15 A still further embodiment of the process for preparing an olefin polymer according to the invention comprises preparing a tapered polymer or an olefin block copolymer by the above process and then bringing the resulting (co)polymer into contact with a functional  
20 group-containing compound to prepare a tapered polymer or an olefin block copolymer having a functional group at the terminal.

- A still further embodiment of the process for preparing an olefin polymer according to the invention  
25 comprises polymerizing an olefin in the presence of a

polymerization catalyst which promotes living polymerization of an olefin and further conducting olefin polymerization by the use of a catalyst obtained by cleaving a bond produced in the system between the catalyst and the resulting polymer chain by means of chain transfer reaction.

The chain transfer reaction can be promoted by the use of at least one compound selected from, for example, hydrogen, an organoaluminum compound, an organoboron compound, an organozinc compound, an organosilicon compound, an organocadmium compound and an organolead compound.

The olefin polymerization catalyst used in the above process is, for example, an olefin polymerization catalyst comprising the above-mentioned transition metal compound. The polymer produced in the above process is, for example, the monodisperse polyolefin, the olefin copolymer, the tapered polymer or the olefin block copolymer.

In the process for preparing an olefin polymer, it is preferable that the olefin polymer obtained before the chain transfer reaction and/or the olefin polymer obtained after the chain transfer reaction is the monodisperse polyolefin, the olefin copolymer, the tapered polymer or the olefin block copolymer, and it is

more preferable that the olefin polymer obtained before the chain transfer reaction and the olefin polymer obtained after the chain transfer reaction are each the monodisperse polyolefin, the olefin copolymer, the tapered polymer or the olefin block copolymer. The olefin polymer obtained before the chain transfer reaction and the olefin polymer obtained after the chain transfer reaction may be the same as each other.

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BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is an explanatory view showing steps for preparing an olefin polymerization catalyst which is occasionally used in the present invention.

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BEST MODE FOR CARRYING OUT THE INVENTION

The olefin polymers according to the invention and the processes for preparing the polymers are described in detail hereinafter.

The meaning of the term "polymerization" used herein is not limited to "homopolymerization" but may comprehend "copolymerization". Also, the meaning of the term "polymer" used herein is not limited to "homopolymer" but may comprehend "copolymer".

The olefin polymer (monodisperse polyolefin) in one embodiment of the invention is a polymer of at least one

olefin selected from olefins of 2 to 20 carbon atoms (sometimes referred to as "olefins" hereinafter). This olefin polymer may be a polymer of one olefin selected from olefins of 2 to 20 carbon atoms or may be a random copolymer or a block copolymer of two or more olefins selected from olefins of 2 to 20 carbon atoms.

Examples of the olefins of 2 to 20 carbon atoms include:

- straight-chain or branched  $\alpha$ -olefins of 2 to 20 carbon atoms, such as ethylene, propylene, 1-butene, 1-pentene, 3-methyl-1-butene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene; and
- cycloolefins of 3 to 20 carbon atoms, such as cyclopentene, cycloheptene, norbornene, 5-methyl-2-norbornene, tetracyclododecene and 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene.

Vinylcyclohexane, dienes and polyenes are also employable as the olefins of 2 to 20 carbon atoms.

As the dienes or the polyenes, cyclic or chain compounds having 4 to 20 carbon atoms and two or more double bonds can be mentioned. Examples of such compounds include butadiene, isoprene, 4-methyl-1,3-pentadiene, 1,3-pentadiene, 1,4-pentadiene, 1,5-hexadiene,

**5** 8-methyl-1,7-nonadiene and 5,9-dimethyl-1,4,8-decatriene.

10 ethylstyrene, m-ethylstyrene and p-ethylstyrene, 3-phenylpropylene, 4-phenylpropylene and  $\alpha$ -methylstyrene.

The above olefins can be used singly or in combination of two or more kinds.

15 carbon and hydrogen are also employable in the invention.

Examples of such monomers include:

20 carboxylic acids or anhydrides thereof, such as bicyclo(2,2,1)-5-heptene-2,3-dicarboxylic acid, and metallic salts thereof, such as sodium salts, potassium salts, lithium salts, zinc salts, magnesium salts and calcium salts thereof;

$\alpha,\beta$ -unsaturated carboxylic esters, such as methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, tert-butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, 5 ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate and isobutyl methacrylate;

vinyl esters, such as vinyl acetate, vinyl propionate, vinyl caproate, vinyl caprate, vinyl laurate, 10 vinyl stearate and vinyl trifluoroacetate;

unsaturated glycidyls, such as glycidyl acrylate, glycidyl methacrylate and monoglycidyl itaconate;

halogenated olefins, such as vinyl fluoride, vinyl chloride, vinylidene chloride, vinyl bromide and vinyl 15 iodide;

unsaturated cyano compounds, such as acrylonitrile and methacrylonitrile;

unsaturated amides, such as acrylamide, methacrylamide and N,N-dimethylacrylamide;

20 unsaturated ketones, such as vinyl methyl ketone and vinyl ethyl ketone;

unsaturated ethers, such as methyl vinyl ether and ethyl vinyl ether;

functional group-containing styrene derivatives, 25 such as methoxystyrene, ethoxystyrene, vinyl benzoate,

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methylvinyl benzoate, vinylbenzyl acetate, hydroxystyrene, o-chlorostyrene, p-chlorostyrene and divinylbenzene; and vinyl group-containing heterocyclic compounds, such as N-vinylpyrrolidone, N-vinylcarbazole and vinylpyridine.

- 5       At least one olefin selected from the olefins employable in the invention is an olefin consisting of only carbon and hydrogen. There is no specific limitation on the quantity ratio of the olefin consisting of only carbon and hydrogen to the whole olefins, but for  
10       example, the ratio is not less than 5 % by mol and not more than 100 % by mol based on the whole olefins. By the expression "at least one olefin" is meant that at least one kind of an olefin consisting of only carbon and hydrogen is contained in the whole olefin polymer of the  
15       invention, and in case of, for example, an olefin polymer composed of plural polymer blocks, the olefin consisting of only carbon and hydrogen may be contained in any one of the polymer blocks.

- 20       The monodisperse polyolefin desirably has a number-average molecular weight of not less than 500, preferably 500 to 10,000,000, more preferably 1,000 to 5,000,000, and Mw/Mn of not more than 1.5, preferably not more than 1.3.

- 25       The weight-average molecular weight, number-average molecular weight and Mw/Mn (Mw: weight-average molecular



weight, Mn: number-average molecular weight) are measured in an orthodichlorobenzene solvent at 140°C by means of GPC (gel permeation chromatography). The polymer molecular weight obtained is converted to a molecular weight in terms of polystyrene by a universal method. When the resulting polymer is monodisperse polyethylene or a monodisperse ethylene/propylene copolymer, the molecular weight is calculated in terms of polyethylene, and when the resulting polymer is another polymer (tapered polymer, olefin block copolymer), the molecular weight is calculated in terms of polypropylene. The parameters used are as follows.

Polystyrene standard sample:  $K=0.000137$ ,  $\alpha=0.686$

Polyethylene:  $K=0.000326$ ,  $\alpha=0.77$

Polypropylene:  $K=0.0001$ ,  $\alpha=0.8$

The melting point of the resulting polymer is measured in a stream of nitrogen under the heating rate conditions of 10°C/min using a differential scanning calorimeter (DSC).

The  $^{13}\text{C}$ -NMR measurement and analysis can be carried out in accordance with a method hitherto known. Literatures on the  $^{13}\text{C}$ -NMR measurement and analysis are given below.

- 1) L.P. Lindeman, J.Q. Adams, Anal. Chem., 43, 1245 (1971)

- 2) F.A. Bovey, M.C. Sacchi, A. Zambelli,  
Macromolecules, 7, 752 (1974)
- 3) J.C. Randall, Macromolecules, 11, 33 (1978)
- 4) A. Zambelli, P. Locatelli, G. Bajo,  
5 Macromolecules, 12, 154 (1979)
- 5) Y. Doi, Macromolecules, 12, 248 (1979)
- 6) N. Kashiwa, A. Mizuno, S. Minami, Polym. Bull.,  
12, 105 (1984)
- 7) P. Ammendola, L. Oliva, G. Gianotti, A. Zambelli,  
10 Macromolecules, 18, 1407 (1985)
- 8) T. Tsutsui, A. Mizuno, N. Kashiwa, Polymer, 30,  
428 (1989)
- 9) T. Tsutsui, N. Ishimaru, A. Mizuno, A. Toyota, N.  
Kashiwa, Polymer, 30, 1350 (1989)
- 15 Preferred examples of the monodisperse polyolefins  
according to the invention include polyethylene, HDPE,  
LLDPE, polypropylene, polybutene, a homopolymer of 1-  
pentene, 1-hexene, 1-octene, 1-decene or the like, a  
copolymer of ethylene and propylene, a copolymer of  
20 ethylene and an olefin of 4 to 20 carbon atoms, and a  
copolymer of propylene and an olefin of 4 to 20 carbon  
atoms. In these examples, polyethylene is an ethylene  
polymer having a comonomer content of less than 0.01 % by  
mol, HDPE is an ethylene copolymer containing as a  
25 comonomer component an olefin of 3 to 8 carbon atoms,

- preferably propylene, 1-butene or 1-hexene, in an amount of not less than 0.01 % by mol and less than 3 % by mol, and LLDPE is an ethylene copolymer containing as a comonomer component an olefin of 3 to 8 carbon atoms,
- 5 preferably propylene, 1-butene or 1-hexene, in an amount of not less than 3 % by mol and less than 10 % by mol. Examples of the olefins of 4 to 20 carbon atoms include  $\alpha$ -olefins, such as 1-butene, 1-pentene, 1-hexene, 1-octene and 1-decene; dienes, such as butadiene, isoprene,
- 10 1,4-pentadiene, 1,5-hexadiene and 1,7-octadiene; aromatic vinyl compounds, such as styrene; and cycloolefin compounds, such as tetracyclododecene, norbornene and methyl norbornene. When the comonomer is an olefin of 3 to 8 carbon atoms, the comonomer content is not less than
- 15 10 % by mol, and in other cases, the comonomer content is not less than 0.01 % by mol.

Of the above examples, the copolymers may contain one comonomer or may contain two or more comonomers.

- Of the above polyolefins, preferable are
- 20 polyethylene, HDPE, LLDPE, polypropylene, polybutene, an ethylene/propylene copolymer, an ethylene/butene copolymer and an ethylene/hexene copolymer, and particularly preferable are HDPE, LLDPE, polypropylene, polybutene, an ethylene/propylene copolymer, an

ethylene/butene copolymer and an ethylene/hexene copolymer.

The monodisperse polyolefin of the invention is preferably a polymer of ethylene which has a number-  
5 average molecular weight of not less than 110,000, preferably 110,000 to 10,000,000, more preferably 150,000 to 5,000,000, and Mw/Mn of not more than 1.5, preferably not more than 1.3, or a polymer of at least one olefin selected from olefins of 3 to 20 carbon atoms which has a  
10 number-average molecular weight of not less than 500, preferably 500 to 10,000,000, more preferably 1,000 to 5,000,000, Mw/Mn of not more than 1.5, preferably not more than 1.3, and a melting point of not lower than 70°C.

In case of a polymer of propylene or 1-butene, this  
15 polymer preferably has a number-average molecular weight of not less than 500, preferably 500 to 10,000,000, more preferably 1,000 to 5,000,000, Mw/Mn of not more than 1.5, preferably not more than 1.3, and a racemic diad (r), as measured by  $^{13}\text{C}$ -NMR, of not less than 0.85, preferably  
20 not less than 0.90.

In case of an ethylene/propylene copolymer, the ethylene content is preferably not less than 60 % by mol, more preferably not less than 70 % by mol.

The monodisperse polyolefin of the invention may be  
25 bonded to other structural parts within limits not

detrimental to the objects of the invention. The polymer of the invention may be a graft modified polymer.

The olefin polymer according to the invention is, for example, a copolymer of at least two olefins selected from olefins of 2 to 20 carbon atoms, which has a number-average molecular weight of not less than 500, preferably 500 to 10,000,000, more preferably 1,000 to 5,000,000, and which is a so-called tapered polymer containing a segment wherein composition of two or more monomers continuously changes.

The "tapered polymer" used herein is a polymer in which the comonomer composition gradually changes from one end to the other end of the polymer chain. This polymer can be synthesized by polymerizing two or more monomers (e.g., ethylene and propylene) in a perfect living polymerization system wherein the chain transfer reaction does not substantially take place. When the living properties of the polymerization system is insufficient, obtainable is not a perfect tapered polymer but a mixture of copolymers having different compositions. The living properties of the polymerization system is judged by a molecular weight distribution ( $M_w/M_n$ ) of the resulting polymer. When the living properties of the polymerization system is high and a perfect tapered polymer is produced, the value of  $M_w/M_n$  is preferably not

more than 2.5, more preferably not more than 1.8, still more preferably not more than 1.5.

In the above polymer, the two or more monomers are selected from olefins of 2 to 20 carbon atoms.

- 5 Specifically, they are preferably selected from ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene and 1-octene, and they are more preferably selected from ethylene, propylene and 1-butene. One of the monomers is still more preferably ethylene, and the ethylene content
- 10 is particularly preferably not less than 30 % by mol.

- Examples of the tapered polymers include an ethylene/propylene tapered polymer, an ethylene/butene tapered polymer, an ethylene/hexene tapered polymer, a propylene/butene tapered polymer and a propylene/hexene
- 15 tapered polymer.

- The tapered polymer of the invention may be bonded to other structural parts within limits not detrimental to the objects of the invention, with the proviso that it has the above structure. The polymer of the invention
- 20 may be a graft modified polymer.

The olefin polymer according to the invention is, for example, the following polymer.

- An olefin polymer which is a polymer consisting of two or more kinds of monomer units, i.e., a monomer unit
- 25  $M_1$  derived from an olefin of 2 to 20 carbon atoms and at

least one monomer unit  $M_2$  that is different from the monomer unit  $M_1$ , and which has the following properties:

$[M_1 \cdot M_2]$ ,  $[M_1 \cdot M_1]$ ,  $[M_2 \cdot M_2]$ ,  $[M_1]$  and  $[M_2]$ , as

measured by  $^{13}\text{C}$ -NMR, satisfy the following relations:

$$5 \quad 1 > [M_1 \cdot M_2] / (2 \times [M_1] \times [M_2]) \quad (A)$$

$$1 > [M_1 \cdot M_2]^2 / (4 \times [M_1 \cdot M_1] \times [M_2 \cdot M_2]) \quad (B)$$

- wherein  $[M_1]$  is a molar fraction of the monomer unit  $M_1$ ,  $[M_2]$  is a molar fraction of the monomer unit  $M_2$ ,  $[M_1 \cdot M_2]$  is a molar fraction of a unit in which the monomer unit  $M_1$  and the monomer unit  $M_2$  are adjacent to each other,  $[M_1 \cdot M_1]$  is a molar fraction of a unit in which the monomer unit  $M_1$  and the monomer unit  $M_1$  are adjacent to each other, and  $[M_2 \cdot M_2]$  is a molar fraction of a unit in which the monomer unit  $M_2$  and the monomer unit  $M_2$  are adjacent to each other, with the proviso that  $[M_1] + [M_2] = 1.0$  and  $[M_1 \cdot M_2] + [M_1 \cdot M_1] + [M_2 \cdot M_2] = 1.0$ .

- When the monomer unit  $M_1$  and the monomer unit  $M_2$  are contained in the polymer chain at statistically random, the probability of occurrence of  $[M_1 \cdot M_2]$  becomes  $2 \times [M_1] \times [M_2]$ . The reason of multiplication by 2 is that  $[M_1 \cdot M_2]$  is strictly a molar fraction of units of the total of the  $M_1$ - $M_2$  units and the  $M_2$ - $M_1$  units. The relation (A) indicates that the units wherein the monomer unit  $M_1$  and the monomer unit  $M_2$  are adjacent are contained in amounts smaller than those in the case where

they are contained at statistically random. This means that a portion of high content of the monomer units  $M_1$  and a portion of high content of the monomer units  $M_2$  coexist in one polymer chain, and this phenomenon is

5 observed in a tapered polymer or a block polymer.

The structure of the olefin copolymer of the invention is precisely controlled, so that the  $M_w/M_n$  of the copolymer is usually not more than 2.5, preferably not more than 2.0, more preferably not more than 1.8, 10 still more preferably not more than 1.6, particularly preferably not more than 1.5, most preferably not more than 1.3.

When a tapered polymer or a block polymer satisfying the relation (A) is intended to be synthesized by the prior technique, there is a possibility that a polymer apparently satisfying the relation (A) can be synthesized by changing the feed ratio between the monomer unit  $M_1$  and the monomer unit  $M_2$  with time during the polymerization. In this case, however, the polymerization reactivities of the monomer unit  $M_1$  and the monomer unit  $M_2$  are different from each other, and consequently the reactivities of the feed monomers change with time. As a result, a small value of  $M_w/M_n$  is not obtained, differently from the present invention.



On the other hand, when a polymer of small  $M_w/M_n$  is intended to be prepared by the prior technique, the feed ratio between the monomer unit  $M_1$  and the monomer unit  $M_2$  needs to be kept constant during the polymerization in order to prevent change of the reactivities of the feed monomers with time, so that the probability of occurrence of  $[M_1 \cdot M_2]$  becomes equal to  $2 \times [M_1] \times [M_2]$ , and it becomes impossible to satisfy the relation (A).

In the present invention, it is possible to precisely control the polymer structure even when the reactivities of the feed monomers change with time. The relation (A) is preferably the following relation (A-2), more preferably the following relation (A-3).

$$0.95 \geq [M_1 \cdot M_2] / (2 \times [M_1] \times [M_2]) \quad (A-2)$$

$$0.90 \geq [M_1 \cdot M_2] / (2 \times [M_1] \times [M_2]) \quad (A-3)$$

The relation (B) is a relation to verify the contents described with respect to the relation (A) with much higher accuracy.

As described above,  $[M_1 \cdot M_2]$  is strictly a molar fraction of units of the total of the  $M_1$ - $M_2$  units and the  $M_2$ - $M_1$  units, so that the probability of occurrence of the  $M_1$ - $M_2$  unit wherein the monomer unit  $M_1$  is followed by the monomer unit  $M_2$  and the probability of occurrence of the  $M_2$ - $M_1$  unit wherein the monomer unit  $M_2$  is followed by the monomer unit  $M_1$  both become  $[M_1 \cdot M_2] / 2$ . When the terminal

of the polymer is the monomer unit  $M_1$  and after this monomer unit the monomer unit  $M_1$  or the monomer unit  $M_2$  is inserted to produce a  $M_1-M_1$  unit or a  $M_1-M_2$  unit and besides when the polymerization proceeds at statistically random, the ratio between occurrences of those units agrees with the ratio between  $[M_1]$  and  $[M_2]$ . That is, the molar fractions satisfy the following relation (B-0-1).

$$([M_1 \cdot M_2] / 2) / [M_1 \cdot M_1] = [M_2] / [M_1] \quad (B-0-1)$$

On the other hand, when the terminal of the polymer is the monomer unit  $M_2$  and after this monomer unit the monomer unit  $M_1$  or the monomer unit  $M_2$  is inserted to produce a  $M_2-M_1$  unit or a  $M_2-M_2$  unit and besides when the polymerization proceeds at statistically random, the ratio between occurrences of those units agrees with the ratio between  $[M_1]$  and  $[M_2]$ . That is, the molar fractions satisfy the following relation (B-0-2).

$$([M_1 \cdot M_2] / 2) / [M_2 \cdot M_2] = [M_1] / [M_2] \quad (B-0-2)$$

That is, when the polymerization proceeds at statistically random, the following relation (B-0) wherein both sides of the relations (B-0-1) and (B-0-2) are multiplied is given.

$$1 = [M_1 \cdot M_2]^2 / (4 \times [M_1 \cdot M_1] \times [M_2 \cdot M_2]) \quad (B-0)$$

The aforesaid relation (B) indicates that the units wherein the monomer unit  $M_1$  and the monomer unit  $M_2$  are

adjacent are contained in amounts smaller than those in the case where they are produced at statistically random. This means that the probability of continuous insertion of the same kind of comonomers at the terminal of the

5 polymer is higher than the probability of insertion of different kinds of comonomers at the terminal of the polymer and that a tapered polymer or a block polymer can be synthesized with precisely controlling the structure.

The structure of the olefin copolymer of the

10 invention is precisely controlled, so that the Mw/Mn of the copolymer is usually not more than 2.5, preferably not more than 2.0, more preferably not more than 1.8, still more preferably not more than 1.6, particularly preferably not more than 1.5, most preferably not more

15 than 1.4. The relation (B) is preferably the following relation (B-2), more preferably the following relation (B-3), still more preferably the following relation (B-4), much more preferably the following relation (B-5), particularly preferably the following relation (B-6),

20 most preferably the following relation (B-7).

$$0.95 > [M_1 \cdot M_2]^2 / (4 \times [M_1 \cdot M_1] \times [M_2 \cdot M_2]) \quad (B-2)$$

$$0.90 > [M_1 \cdot M_2]^2 / (4 \times [M_1 \cdot M_1] \times [M_2 \cdot M_2]) \quad (B-3)$$

$$0.85 > [M_1 \cdot M_2]^2 / (4 \times [M_1 \cdot M_1] \times [M_2 \cdot M_2]) \quad (B-4)$$

$$0.80 > [M_1 \cdot M_2]^2 / (4 \times [M_1 \cdot M_1] \times [M_2 \cdot M_2]) \quad (B-5)$$

25  $0.75 > [M_1 \cdot M_2]^2 / (4 \times [M_1 \cdot M_1] \times [M_2 \cdot M_2]) \quad (B-6)$

$$0.70 > [M_1 \cdot M_2]^2 / (4 \times [M_1 \cdot M_1] \times [M_2 \cdot M_2]) \quad (B-7)$$

The reason why a polymer having a small Mw/Mn value and satisfying the relation (B), such as the tapered polymer of the invention, cannot be produced by the prior  
5 technique is the same as the reason why a polymer satisfying the relation (A) cannot be produced.

It is detected by  $^{13}\text{C}$ -NMR that in the tapered polymer out of the olefin copolymers satisfying the relations (A) and (B) and having  $M_w/M_n$  of not more than 2.5, an isolated monomer unit  $M_1$  and a sequence of two or more continuous monomer units  $M_1$  are both present in the polymer chain. Such a tapered polymer structure was not analyzed by  $^{13}\text{C}$ -NMR in the prior art, and it has been made clear for the first time by the technique of the present invention which is capable of promoting extremely precise polymerization.

On the other hand, in the block polymer the isolated monomer unit  $M_1$  is not detected but only a sequence of two or more continuous monomer units  $M_1$  is detected.

20 In the tapered polymer structure made clear by the present invention for the first time, it is preferable that a sequence of two continuous monomer units  $M_1$  and a sequence of three or more continuous monomer units  $M_1$  are detected. That is, it is preferable that three units of

25 an isolated monomer unit  $M_1$ , a unit composed of two

continuous monomer units  $M_1$  and a unit composed of three or more monomer units  $M_1$  are detected by  $^{13}\text{C}$ -NMR at the same time.

The monomer unit  $M_1$  and the monomer unit  $M_2$  are  
5 derived from the monomers previously given as examples of the olefins of 2 to 20 carbon atoms.

The monomer unit  $M_1$  is preferably derived from ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene or 1-octene, and is more preferably derived from  
10 ethylene. The monomer unit  $M_2$  is preferably derived from propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene or 1-octene, and is more preferably derived from propylene or 1-butene.

When the monomer unit  $M_1$  is an ethylene unit, it is  
15 preferable that three units of an isolated monomer unit  $M_1$ , a unit composed of two continuous monomer units  $M_1$  and a unit composed of three or more monomer units  $M_1$  are detected by  $^{13}\text{C}$ -NMR at the same time. It is also preferable that an isolated monomer unit  $M_2$  and a unit  
20 composed of two or more continuous monomer units  $M_2$  are detected at the same time. That is, it is preferable that a sequence of two or more continuous methylene groups is detected by  $^{13}\text{C}$ -NMR and sequences of one, two, three, four, five and six or more methylene groups are  
25 all detected. It is more preferable that the molar

fractions of the sequences of one, two, three, four, five and six or more methylene groups are detected as different values.

The  $^{13}\text{C}$ -NMR measurement and analysis can be carried  
5 out in accordance with a method hitherto known, as previously described.

The olefin copolymer can be favorably used for various molding materials for films, sheets and blow molded products, various additives such as  
10 compatibilizing agent and modifier, coating materials and adhesives. The use application will be described later.

The process for preparing the olefin copolymer of the invention will be described later.

The olefin copolymer of the invention may have a  
15 functional group at the terminal of the main chain. The olefin copolymer of the invention may be bonded to other structural parts within limits not detrimental to the objects of the invention, with the proviso that it has the above structure. The polymer of the invention may be  
20 a graft modified polymer.

As the functional group, an aromatic hydrocarbon group, a halogen atom, an oxygen-containing group, a nitrogen-containing group, a sulfur-containing group, a phosphorus-containing group, a metal atom-containing  
25 group or the like is preferable.

Examples of the aromatic hydrocarbon groups include phenyl, naphthyl, tolyl, biphenyl and anthryl.

Examples of the halogen atoms include fluorine, chlorine, bromine and iodine.

- 5        The oxygen-containing group is, for example, a group containing 1 to 5 oxygen atoms, but the later-described heterocyclic compound residue is not included in this group. A group containing a nitrogen atom, a sulfur atom, a phosphorus atom or a halogen atom, said atom being
- 10       directly bonded to the oxygen atom, is not included either. Examples of the oxygen-containing groups include hydroxyl group; alkoxy groups, such as methoxy, ethoxy, propoxy and butoxy; aryloxy groups, such as phenoxy, methylphenoxy, dimethylphenoxy and naphthoxy; arylalkoxy
- 15       groups, such as phenylmethoxy and phenylethoxy; acetoxy group; carbonyl group; carboxyl group; ester group; and acetyl group. When the oxygen-containing group contains carbon atom, the number of carbon atoms is in the range of usually 1 to 30, preferably 1 to 20.
- 20       The nitrogen-containing group is, for example, a group containing 1 to 5 nitrogen atoms, but the later-described heterocyclic compound residue is not included in this group. Examples of the nitrogen-containing groups include amino group; alkylamino groups, such as
- 25       methylamino, dimethylamino, ethylamino, propylamino,

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butylamino and cyclohexylamino; and arylamino groups, such as phenylamino, tolylamino and naphthylamino.

- The sulfur-containing group is, for example, a group containing 1 to 5 sulfur atoms, but the later-described
- 5 heterocyclic compound residue is not included in this group. Examples of the sulfur-containing groups include sulfonato groups, such as methylsulfonato, trifluoromethanesulfonato, phenylsulfonato, benzylsulfonato, p-toluenesulfonato,
- 10 trimethylbenzenesulfonato, triisobutylbenzenesulfonato, p-chlorobenzenesulfonato and pentafluorobenzenesulfonato; sulfinato groups, such as methylsulfinato, phenylsulfinato, benzylsulfinato, p-toluenesulfinato, trimethylbenzenesulfinato and pentafluorobenzenesulfinato;
- 15 alkylthio groups; and arylthio groups. When the sulfur-containing group contains carbon atom, the number of carbon atoms is in the range of usually 1 to 30, preferably 1 to 20.

- The phosphorus-containing group is, for example, a
- 20 group containing 1 to 5 phosphorus atoms, and examples thereof include trialkylphosphine groups, such as trimethylphosphine, tributylphosphine and tricyclohexylphosphine; triarylphosphine groups, such as triphenylphosphine and tritolyphosphine; phosphite
- 25 groups (phosphido groups), such as methylphosphite,



ethylphosphite and phenylphosphite; phosphonic acid group; and phosphinic acid group.

The metal atom-containing group is, for example, a group containing an atom of silicon, aluminum, boron, zinc or magnesium, or a metal atom such as lithium, and examples thereof include a silicon-containing group, an aluminum-containing group, a boron-containing group, a zinc-containing group, a magnesium-containing group and a lithium atom.

The silicon-containing group is, for example, a group containing 1 to 5 silicon atoms. Examples of the silicon-containing groups include hydrocarbon-substituted silyl groups, such as phenylsilyl, diphenylsilyl, trimethylsilyl, triethylsilyl, tripropylsilyl, tricyclohexylsilyl, triphenylsilyl, tritolylsilyl, trinaphthylsilyl and methyldiphenylsilyl; alkyl-substituted silyl ether groups, such as trimethylsilyl ether; silicon-substituted alkyl groups, such as trimethylsilylmethyl; silicon-substituted aryl groups, such as trimethylsilylphenyl; and hydrocarbon-substituted siloxy groups, such as trimethylsiloxy. Of the hydrocarbon-substituted silyl groups, trialkylsilyl groups, such as trimethylsilyl, tripropylsilyl and tricyclohexylsilyl, are preferable.

The aluminum-containing group is, for example, a group containing 1 to 5 aluminum atoms. An example of the aluminum-containing group is  $-AlR_2$  group (R is hydrogen, an alkyl group, an aryl group which may have a substituent, a halogen atom or the like).

The boron-containing group is, for example, a group containing 1 to 5 boron atoms. An example of the boron-containing group is  $-BR_2$  group (R is hydrogen, an alkyl group, an aryl group which may have a substituent, a halogen atom or the like).

The zinc-containing group is, for example, a group containing 1 to 3 zinc atoms. An example of the zinc-containing group is  $-ZnR$  group (R is hydrogen, an alkyl group, an aryl group which may have a substituent, a halogen atom or the like).

The magnesium-containing group is a group containing 1 to 3 magnesium atoms. An example of the magnesium-containing group is  $-MgR$  group (R is hydrogen, an alkyl group, an aryl group which may have a substituent, a halogen atom or the like).

Examples of the olefin polymers having a functional group at the terminal of the main chain include polymers having a halogen atom, a phenyl group, a hydroxyl group, an alkoxy group, a carbonyl group, a carboxyl group, an ester group, an acetyl group, an alkylamino group, a

- trialkylsilyl group, a trimethylsiloxy group, a dialkylaluminum group, a dialkylboron group, an alkylzinc group, lithium or the like at the terminals of polyethylene, HDPE, LLDPE, polypropylene, polybutene, a
- 5 homopolymer of 1-pentene, 1-hexene, 1-octene, 1-decene or the like, a copolymer of ethylene and propylene, a copolymer of ethylene and an olefin of 4 to 20 carbon atoms (e.g.,  $\alpha$ -olefins, such as 1-butene, 1-pentene, 1-hexene, 1-octene and 1-decene; dienes, such as butadiene,
- 10 isoprene, 1,4-pentadiene, 1,5-hexadiene and 1,7-octadiene; aromatic vinyl compounds, such as styrene; cycloolefin compounds, such as tetracyclododecene, norbornene and methyl norbornene), a copolymer of propylene and the above-mentioned olefin of 4 to 20
- 15 carbon atoms, and the aforesaid tapered polymer.

Of these, particularly preferable are polymers having a chlorine atom, a bromine atom, an iodine atom, a hydroxyl group or an alkylzinc group at the terminals of polyethylene, HDPE, LLDPE, polypropylene, polybutene, an

20 ethylene/propylene copolymer, an ethylene/butene copolymer and an ethylene/hexene copolymer.

The olefin polymer having a functional group at the terminal of the main chain can be favorably used for various additives such as compatibilizing agent and

modifier, coating materials and adhesives. The use application of the polymer will be described later.

The process for preparing the olefin polymer having a functional group at the terminal of the main chain will  
5 be described later.

The olefin polymer in another embodiment of the invention is an olefin block copolymer comprising:

- (i) a polymer block obtained from at least one olefin selected from olefins of 2 to 20 carbon atoms, and
- 10 (ii) a polymer block that is obtained from at least one olefin selected from olefins of 2 to 20 carbon atoms and is different from the polymer block (i).

The polymer blocks different from each other are those different in at least one of primary structures of  
15 polymers, such as monomer type, comonomer type, comonomer composition, comonomer content, comonomer configuration and stereoregularity.

The polymer blocks (i) and (ii) may be each a polymer of one olefin selected from olefins of 2 to 20  
20 carbon atoms or may be a random copolymer of two or more olefins selected from olefins of 2 to 20 carbon atoms.

The olefin block copolymer may further have single or plural polymer blocks (iii) in addition to the polymer block (i) and the polymer block (ii). In this case, the  
25 block copolymer takes a form of (i)-(ii)-(iii)<sub>n</sub>, wherein



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- 15

homopolymer of propylene, 1-butene, 1-hexene or 1-octene.

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of not less than 110,000, preferably 110,000 to 10,000,000, more preferably 150,000 to 5,000,000, and Mw/Mn of not more than 1.5, preferably not more than 1.3.

The above-mentioned olefin polymer is, for example,  
5 a polymer wherein an arbitrary number of polymer blocks obtained from at least one olefin selected from olefins of 2 to 20 carbon atoms are bonded, the number-average molecular weight (Mn) of the whole polymers is not less than 500, preferably 500 to 10,000,000, more preferably  
10 1,000 to 5,000,000, adjacent polymer blocks are different from each other, the number-average molecular weight of each polymer block is not less than 100, preferably 100 to 9,999,900, more preferably 500 to 4,999,500, and Mw/Mn of each polymer block is not more than 2.5.

15 In the present invention, the number of polymer blocks is an integer of 2 or more, usually 2 to 10, preferably 2 to 6, particularly preferably 2 to 4.

In case of a diblock polymer in which the number of polymer blocks is 2, Mw/Mn is preferably less than 1.35,  
20 more preferably less than 1.30.

In case of a triblock polymer in which the number of polymer blocks is 3, Mw/Mn is preferably less than 1.80, more preferably less than 1.50.

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In case of a multiblock polymer in which the number of polymer blocks is 4 or more, Mw/Mn is preferably less than 2.00, more preferably less than 1.80.

In the above olefin block copolymers, each polymer  
5 block is preferably selected from polyethylene, HDPE, LLDPE, a copolymer of ethylene and an olefin selected from olefins of 3 to 20 carbon atoms (including dienes and cycloolefins), ata-polypropylene, iso-polypropylene, syn-polypropylene, a copolymer of propylene and a monomer  
10 selected from olefins of 4 to 20 carbon atoms (including dienes and cycloolefins), and the aforesaid tapered polymer.

Particularly preferable is a diblock polymer or a triblock polymer in which each polymer block is selected  
15 from polyethylene, HDPE, LLDPE, an ethylene/propylene copolymer, an ethylene/butene copolymer, an ethylene/hexene copolymer, an ethylene/octene copolymer, ata-polypropylene, syn-polypropylene, a propylene/butene copolymer, a propylene/hexene copolymer, and the  
20 aforesaid tapered polymer.

Examples of the block polymers are given below. In the following examples, polyethylene-HDPE means an olefin block copolymer wherein a polyethylene block and a HDPE block are bonded, and if the polymer block is a copolymer  
25 of two or more monomers, such as an ethylene/propylene

- copolymer, its monomer configuration may be that of a random copolymer or a tapered polymer.
- polyethylene-HDPE, polyethylene-LLDPE,  
polyethylene-ethylene/propylene copolymer,
- 5 polyethylene-ethylene/butene copolymer,  
polyethylene-ethylene/hexene copolymer,  
polyethylene-ethylene/octene copolymer,  
polyethylene-ata-polypropylene,  
polyethylene-syn-polypropylene,
- 10 polyethylene-propylene/butene copolymer,  
polyethylene-propylene/hexene copolymer,  
HDPE-LLDPE, HDPE-ethylene/propylene copolymer,  
HDPE-ethylene/butene copolymer,  
HDPE-ethylene/hexene copolymer,
- 15 HDPE-ethylene/octene copolymer, HDPE-ata-polypropylene,  
HDPE-syn-polypropylene, HDPE-propylene/butene copolymer,  
HDPE-propylene/hexene copolymer,  
LLDPE-ethylene/propylene copolymer,  
LLDPE-ethylene/butene copolymer,
- 20 LLDPE-ethylene/hexene copolymer,  
LLDPE-ethylene/octene copolymer, LLDPE-ata-polypropylene,  
LLDPE-syn-polypropylene, LLDPE-propylene/butene copolymer,  
LLDPE-propylene/hexene copolymer,  
ethylene/propylene copolymer-ethylene/butene copolymer,
- 25 ethylene/propylene copolymer-ethylene/hexene copolymer,



- ethylene/propylene copolymer-ethylene/octene copolymer,  
ethylene/propylene copolymer-ata-polypropylene,  
ethylene/propylene copolymer-syn-polypropylene,  
ethylene/propylene copolymer-propylene/butene copolymer,  
5 ethylene/propylene copolymer-propylene/hexene copolymer,  
ethylene/butene copolymer-ethylene/hexene copolymer,  
ethylene/butene copolymer-ethylene/octene copolymer,  
ethylene/butene copolymer-ata-polypropylene,  
ethylene/butene copolymer-syn-polypropylene,  
10 ethylene/butene copolymer-propylene/butene copolymer,  
ethylene/butene copolymer-propylene/hexene copolymer,  
ethylene/hexene copolymer-ethylene/octene copolymer,  
ethylene/hexene copolymer-ata-polypropylene,  
ethylene/hexene copolymer-syn-polypropylene,  
15 ethylene/hexene copolymer-propylene/butene copolymer,  
ethylene/hexene copolymer-propylene/hexene copolymer,  
ethylene/octene copolymer-ata-polypropylene,  
ethylene/octene copolymer-syn-polypropylene,  
ethylene/octene copolymer-propylene/butene copolymer,  
20 ethylene/octene copolymer-propylene/hexene copolymer,  
ata-polypropylene-syn-polypropylene,  
ata-polypropylene-propylene/butene copolymer,  
ata-polypropylene-propylene/hexene copolymer,  
syn-polypropylene-propylene/butene copolymer,  
25 syn-polypropylene-propylene/hexene copolymer,

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propylene/butene copolymer-propylene/hexene copolymer,

polyethylene-HDPE-polyethylene,

polyethylene-LLDPE-polyethylene,

- 5 polyethylene-ethylene/propylene copolymer-polyethylene,  
polyethylene-ethylene/butene copolymer-polyethylene,  
polyethylene-ethylene/hexene copolymer-polyethylene,  
polyethylene-ethylene/octene copolymer-polyethylene,  
polyethylene-ata-polypropylene-polyethylene,  
10 polyethylene-syn-polypropylene-polyethylene,  
polyethylene-propylene/butene copolymer-polyethylene,  
polyethylene-propylene/hexene copolymer-polyethylene,  
HDPE-polyethylene-HDPE, HDPE-LLDPE-HDPE,  
HDPE-ethylene/propylene copolymer-HDPE,  
15 HDPE-ethylene/butene copolymer-HDPE,  
HDPE-ethylene/hexene copolymer-HDPE,  
HDPE-ethylene/octene copolymer-HDPE,  
HDPE-ata-polypropylene-HDPE, HDPE-syn-polypropylene-HDPE,  
HDPE-propylene/butene copolymer-HDPE,  
20 HDPE-propylene/hexene copolymer-HDPE,  
LLDPE-polyethylene-LLDPE, LLDPE-HDPE-LLDPE,  
LLDPE-ethylene/propylene copolymer-LLDPE,  
LLDPE-ethylene/butene copolymer-LLDPE,  
LLDPE-ethylene/hexene copolymer-LLDPE,  
25 LLDPE-ethylene/octene copolymer-LLDPE,

- LLDPE-ata-polypropylene-LLDPE,  
LLDPE-syn-polypropylene-LLDPE,  
LLDPE-propylene/butene copolymer-LLDPE,  
LLDPE-propylene/hexene copolymer-LLDPE,
- 5 ethylene/propylene copolymer-polyethylene-  
ethylene/propylene copolymer,  
ethylene/propylene copolymer-HDPE-ethylene/propylene  
copolymer,  
ethylene/propylene copolymer-LLDPE-ethylene/propylene
- 10 copolymer,  
ethylene/propylene copolymer-ethylene/butene copolymer-  
ethylene/propylene copolymer,  
ethylene/propylene copolymer-ethylene/hexene copolymer-  
ethylene/propylene copolymer,
- 15 ethylene/propylene copolymer-ethylene/octene copolymer-  
ethylene/propylene copolymer,  
ethylene/propylene copolymer-ata-polypropylene-  
ethylene/propylene copolymer,  
ethylene/propylene copolymer-syn-polypropylene-
- 20 ethylene/propylene copolymer,  
ethylene/propylene copolymer-propylene/butene copolymer-  
ethylene/propylene copolymer,  
ethylene/propylene copolymer-propylene/hexene copolymer-  
ethylene/propylene copolymer,
- 25 ethylene/butene copolymer-polyethylene-ethylene/butene

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- copolymer,  
ethylene/butene copolymer-HDPE-ethylene/butene copolymer,  
ethylene/butene copolymer-LLDPE-ethylene/butene copolymer,  
ethylene/butene copolymer-ethylene/propylene copolymer-
- 5 ethylene/butene copolymer,  
ethylene/butene copolymer-ethylene/hexene copolymer-  
ethylene/butene copolymer,  
ethylene/butene copolymer-ethylene/octene copolymer-  
ethylene/butene copolymer,
- 10 ethylene/butene copolymer-ata-polypropylene-  
ethylene/butene copolymer,  
ethylene/butene copolymer-syn-polypropylene-  
ethylene/butene copolymer,  
ethylene/butene copolymer-propylene/butene copolymer-
- 15 ethylene/butene copolymer,  
ethylene/butene copolymer-propylene/hexene copolymer-  
ethylene/butene copolymer,  
ethylene/hexene copolymer-polyethylene-ethylene/hexene  
copolymer,
- 20 ethylene/hexene copolymer-HDPE-ethylene/hexene copolymer,  
ethylene/hexene copolymer-LLDPE-ethylene/hexene copolymer,  
ethylene/hexene copolymer-ethylene/propylene copolymer-  
ethylene/hexene copolymer,  
ethylene/hexene copolymer-ethylene/butene copolymer-
- 25 ethylene/hexene copolymer,

- ethylene/hexene copolymer-ethylene/octene copolymer-  
ethylene/hexene copolymer,  
ethylene/hexene copolymer-ata-polypropylene-  
ethylene/hexene copolymer,  
5 ethylene/hexene copolymer-syn-polypropylene-  
ethylene/hexene copolymer,  
ethylene/hexene copolymer-propylene/butene copolymer-  
ethylene/hexene copolymer,  
ethylene/hexene copolymer-propylene/hexene copolymer-  
10 ethylene/hexene copolymer,  
ethylene/octene copolymer-polyethylene-ethylene/octene  
copolymer,  
ethylene/octene copolymer-HDPE-ethylene/octene copolymer,  
ethylene/octene copolymer-LLDPE-ethylene/octene copolymer,  
15 ethylene/octene copolymer-ethylene/propylene copolymer-  
ethylene/octene copolymer,  
ethylene/octene copolymer-ethylene/butene copolymer-  
ethylene/octene copolymer,  
ethylene/octene copolymer-ethylene/hexene copolymer-  
20 ethylene/octene copolymer,  
ethylene/octene copolymer-ata-polypropylene-  
ethylene/octene copolymer,  
ethylene/octene copolymer-syn-polypropylene-  
ethylene/octene copolymer,  
25 ethylene/octene copolymer-propylene/butene copolymer-

- ethylene/octene copolymer,  
ethylene/octene copolymer-propylene/hexene copolymer-  
ethylene/octene copolymer,  
ata-polypropylene-polyethylene-ata-polypropylene,  
5 ata-polypropylene-HDPE-ata-polypropylene,  
ata-polypropylene-LLDPE-ata-polypropylene,  
ata-polypropylene-ethylene/propylene copolymer-ata-  
polypropylene,  
ata-polypropylene-ethylene/butene copolymer-ata-  
10 polypropylene,  
ata-polypropylene-ethylene/hexene copolymer-ata-  
polypropylene,  
ata-polypropylene-ethylene/octene copolymer-ata-  
polypropylene,  
15 ata-polypropylene-syn-polypropylene-ata-polypropylene,  
ata-polypropylene-propylene/butene copolymer-ata-  
polypropylene,  
ata-polypropylene-propylene/hexene copolymer-ata-  
polypropylene,  
20 syn-polypropylene-polyethylene-syn-polypropylene,  
syn-polypropylene-HDPE-syn-polypropylene,  
syn-polypropylene-LLDPE-syn-polypropylene,  
syn-polypropylene-ethylene/propylene copolymer-syn-  
polypropylene,  
25 syn-polypropylene-ethylene/butene copolymer-syn-

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1870 1871 1872 1873 1874 1875 1876 1877 1878 1879 1880 1881 1882 1883 1884 1885 1886 1887 1888 1889 1890 1891 1892 1893 1894 1895 1896 1897 1898 1899 1900 1901 1902 1903 1904 1905 1906 1907 1908 1909 1910 1911 1912 1913 1914 1915 1916 1917 1918 1919 1920 1921 1922 1923 1924 1925 1926 1927 1928 1929 1930 1931 1932 1933 1934 1935 1936 1937 1938 1939 1940 1941 1942 1943 1944 1945 1946 1947 1948 1949 1950 1951 1952 1953 1954 1955 1956 1957 1958 1959 1960 1961 1962 1963 1964 1965 1966 1967 1968 1969 1970 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980 1981 1982 1983 1984 1985 1986 1987 1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023 2024 2025 2026 2027 2028 2029 2030 2031 2032 2033 2034 2035 2036 2037 2038 2039 2040 2041 2042 2043 2044 2045 2046 2047 2048 2049 2050 2051 2052 2053 2054 2055 2056 2057 2058 2059 2060 2061 2062 2063 2064 2065 2066 2067 2068 2069 2070 2071 2072 2073 2074 2075 2076 2077 2078 2079 2080 2081 2082 2083 2084 2085 2086 2087 2088 2089 2090 2091 2092 2093 2094 2095 2096 2097 2098 2099 2100 2101 2102 2103 2104 2105 2106 2107 2108 2109 2110 2111 2112 2113 2114 2115 2116 2117 2118 2119 2120 2121 2122 2123 2124 2125 2126 2127 2128 2129 2130 2131 2132 2133 2134 2135 2136 2137 2138 2139 2140 2141 2142 2143 2144 2145 2146 2147 2148 2149 2150 2151 2152 2153 2154 2155 2156 2157 2158 2159 2160 2161 2162 2163 2164 2165 2166 2167 2168 2169 2170 2171 2172 2173 2174 2175 2176 2177 2178 2179 2180 2181 2182 2183 2184 2185 2186 2187 2188 2189 2190 2191 2192 2193 2194 2195 2196 2197 2198 2199 2200 2201 2202 2203 2204 2205 2206 2207 2208 2209 2210 2211 2212 2213 2214 2215 2216 2217 2218 2219 2220 2221 2222 2223 2224 2225 2226 2227 2228 2229 2230 2231 2232 2233 2234 2235 2236 2237 2238 2239 2240 2241 2242 2243 2244 2245 2246 2247 2248 2249 2250 2251 2252 2253 2254 2255 2256 2257 2258 2259 2260 2261 2262 2263 2264 2265 2266 2267 2268 2269 2270 2271 2272 2273 2274 2275 2276 2277 2278 2279 2280 2281 2282 2283 2284 2285 2286 2287 2288 2289 2290 2291 2292 2293 2294 2295 2296 2297 2298 2299 2300 2301 2302 2303 2304 2305 2306 2307 2308 2309 2310 2311 2312 2313 2314 2315 2316 2317 2318 2319 2320 2321 2322 2323 2324 2325 2326 2327 2328 2329 2330 2331 2332 2333 2334 2335 2336 2337 2338 2339 2340 2341 2342 2343 2344 2345 2346 2347 2348 2349 2350 2351 2352 2353 2354 2355 2356 2357 2358 2359 2360 2361 2362 2363 2364 2365 2366 2367 2368 2369 2370 2371 2372 2373 2374 2375 2376 2377 2378 2379 2380 2381 2382 2383 2384 2385 2386 2387 2388 2389 2390 2391 2392 2393 2394 2395 2396 2397 2398 2399 2400 2401 2402 2403 2404 2405 2406 2407 2408 2409 2410 2411 2412 2413 2414 2415 2416 2417 2418 2419 2420 2421 2422 2423 2424 2425 2426 2427 2428 2429 2430 2431 2432 2433 2434 2435 2436 2437 2438 2439 2440 2441 2442 2443 2444 2445 2446 2447 2448 2449 2450 2451 2452 2453 2454 2455 2456 2457 2458 2459 2460 2461 2462 2463 2464 2465 2466 2467 2468 2469 2470 2471 2472 2473 2474 2475 2476 2477 2478 2479 2480 2481 2482 2483 2484 2485 2486 2487 2488 2489 2490 2491 2492 2493 2494 2495 2496 2497 2498 2499 2500 2501 2502 2503 2504 2505 2506 2507 2508 2509 2510 2511 2512 2513 2514 2515 2516 2517 2518 2519 2520 2521 2522 2523 2524 2525 2526 2527 2528 2529 2530 2531 2532 2533 2534 2535 2536 2537 2538 2539 2540 2541 2542 2543 2544 2545 2546 2547 2548 2549 2550 2551 2552 2553 2554 2555 2556 2557 2558 2559 2560 2561 2562 2563 2564 2565 2566 2567 2568 2569 2570 2571 2572 2573 2574 2575 2576 2577 2578 2579 2580 2581 2582 2583 2584 2585 2586 2587 2588 2589 2590 2591 2592 2593 2594 2595 2596 2597 2598 2599 2600 2601 2602 2603 2604 2605 2606 2607 2608 2609 2610 2611 2612 2613 2614 2615 2616 2617 2618 2619 2620 2621 2622 2623 2624 2625 2626 2627 2628 2629 2630 2631 2632 2633 2634 2635 2636 2637 2638 2639 2640 2641 2642 2643 2644 2645 2646 2647 2648 2649 2650 2651 2652 2653 2654 2655 2656 2657 2658 2659 2660 2661 2662 2663 2664 2665 2666 2667 2668 2669 2670 2671 2672 2673 2674 2675 2676 2677 2678 2679 2680 2681 2682 2683 2684 2685 2686 2687 2688

polypropylene,

syn-polypropylene-ethylene/hexene copolymer-syn-

polypropylene,

syn-polypropylene-ethylene/octene copolymer-syn-

5 polypropylene,

syn-polypropylene-ata-polypropylene-syn-polypropylene,

syn-polypropylene-propylene/butene copolymer-syn-

polypropylene,

syn-polypropylene-propylene/hexene copolymer-syn-

10 polypropylene,

propylene/butene copolymer-polyethylene-propylene/butene  
copolymer,

propylene/butene copolymer-HDPE-propylene/butene  
copolymer,

15 propylene/butene copolymer-LLDPE-propylene/butene  
copolymer,

propylene/butene copolymer-ethylene/propylene copolymer-  
propylene/butene copolymer,

propylene/butene copolymer-ethylene/butene copolymer-

20 propylene/butene copolymer,

propylene/butene copolymer-ethylene/hexene copolymer-  
propylene/butene copolymer,

propylene/butene copolymer-ethylene/octene copolymer-  
propylene/butene copolymer,

25 propylene/butene copolymer-ata-polypropylene-

- propylene/butene copolymer,  
propylene/butene copolymer-syn-polypropylene-  
propylene/butene copolymer,  
propylene/butene copolymer-propylene/hexene copolymer-
- 5 propylene/butene copolymer,  
propylene/hexene copolymer-polyethylene-propylene/hexene  
copolymer,  
propylene/hexene copolymer-HDPE-propylene/hexene  
copolymer,
- 10 propylene/hexene copolymer-LLDPE-propylene/hexene  
copolymer,  
propylene/hexene copolymer-ethylene/propylene copolymer-  
propylene/hexene copolymer,  
propylene/hexene copolymer-ethylene/butene copolymer-
- 15 propylene/hexene copolymer,  
propylene/hexene copolymer-ethylene/hexene copolymer-  
propylene/hexene copolymer,  
propylene/hexene copolymer-ethylene/octene copolymer-  
propylene/hexene copolymer,
- 20 propylene/hexene copolymer-ata-polypropylene-  
propylene/hexene copolymer,  
propylene/hexene copolymer-syn-polypropylene-  
propylene/hexene copolymer,  
propylene/hexene copolymer-propylene/butene copolymer-
- 25 propylene/hexene copolymer,



- polyethylene-HDPE-LLDPE,  
polyethylene-HDPE-ethylene/propylene copolymer,  
polyethylene-HDPE-ethylene/butene copolymer,  
polyethylene-HDPE-ethylene/hexene copolymer,  
5 polyethylene-HDPE-ethylene/octene copolymer,  
polyethylene-HDPE-ata-polypropylene,  
polyethylene-HDPE-syn-polypropylene,  
polyethylene-HDPE-propylene/butene copolymer,  
polyethylene-HDPE-propylene/hexene copolymer,  
10 polyethylene-LLDPE-HDPE,  
polyethylene-LLDPE-ethylene/propylene copolymer,  
polyethylene-LLDPE-ethylene/butene copolymer,  
polyethylene-LLDPE-ethylene/hexene copolymer,  
polyethylene-LLDPE-ethylene/octene copolymer,  
15 polyethylene-LLDPE-ata-polypropylene,  
polyethylene-LLDPE-syn-polypropylene,  
polyethylene-LLDPE-propylene/butene copolymer,  
polyethylene-LLDPE-propylene/hexene copolymer,  
polyethylene-ethylene/propylene copolymer-HDPE,  
20 polyethylene-ethylene/propylene copolymer-LLDPE,  
polyethylene-ethylene/propylene copolymer-ethylene/butene  
copolymer,  
polyethylene-ethylene/propylene copolymer-ethylene/hexene  
copolymer,  
25 polyethylene-ethylene/propylene copolymer-ethylene/octene

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- copolymer,  
polyethylene-ethylene/propylene copolymer-ata-  
polypropylene,  
polyethylene-ethylene/propylene copolymer-syn-  
5 polypropylene,  
polyethylene-ethylene/propylene copolymer-  
propylene/butene copolymer,  
polyethylene-ethylene/propylene copolymer-  
propylene/hexene copolymer,  
10 polyethylene-ethylene/butene copolymer-HDPE,  
polyethylene-ethylene/butene copolymer-LLDPE,  
polyethylene-ethylene/butene copolymer-ethylene/propylene  
copolymer,  
polyethylene-ethylene/butene copolymer-ethylene/hexene  
15 copolymer,  
polyethylene-ethylene/butene copolymer-ethylene/octene  
copolymer,  
polyethylene-ethylene/butene copolymer-ata-polypropylene,  
polyethylene-ethylene/butene copolymer-syn-polypropylene,  
20 polyethylene-ethylene/butene copolymer-propylene/butene  
copolymer,  
polyethylene-ethylene/butene copolymer-propylene/hexene  
copolymer,  
polyethylene-ethylene/hexene copolymer-HDPE,  
25 polyethylene-ethylene/hexene copolymer-LLDPE,

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- polyethylene-ethylene/hexene copolymer-ethylene/propylene  
copolymer,  
polyethylene-ethylene/hexene copolymer-ethylene/butene  
copolymer,
- 5 polyethylene-ethylene/hexene copolymer-ethylene/octene  
copolymer,  
polyethylene-ethylene/hexene copolymer-ata-polypropylene,  
polyethylene-ethylene/hexene copolymer-syn-polypropylene,  
polyethylene-ethylene/hexene copolymer-propylene/butene
- 10 copolymer,  
polyethylene-ethylene/hexene copolymer-propylene/hexene  
copolymer,  
polyethylene-ethylene/octene copolymer-HDPE,  
polyethylene-ethylene/octene copolymer-LLDPE,
- 15 polyethylene-ethylene/octene copolymer-ethylene/propylene  
copolymer,  
polyethylene-ethylene/octene copolymer-ethylene/butene  
copolymer,  
polyethylene-ethylene/octene copolymer-ethylene/hexene
- 20 copolymer,  
polyethylene-ethylene/octene copolymer-ata-polypropylene,  
polyethylene-ethylene/octene copolymer-syn-polypropylene,  
polyethylene-ethylene/octene copolymer-propylene/butene  
copolymer,
- 25 polyethylene-ethylene/octene copolymer-propylene/hexene

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- copolymer,  
polyethylene-ata-polypropylene-HDPE,  
polyethylene-ata-polypropylene-LLDPE,  
polyethylene-ata-polypropylene-ethylene/propylene
- 5 copolymer,  
polyethylene-ata-polypropylene-ethylene/butene copolymer,  
polyethylene-ata-polypropylene-ethylene/hexene copolymer,  
polyethylene-ata-polypropylene-ethylene/octene copolymer,  
polyethylene-ata-polypropylene-syn-polypropylene,
- 10 polyethylene-ata-polypropylene-propylene/butene copolymer,  
polyethylene-ata-polypropylene-propylene/hexene copolymer,  
polyethylene-syn-polypropylene-HDPE,  
polyethylene-syn-polypropylene-LLDPE,  
polyethylene-syn-polypropylene-ethylene/propylene
- 15 copolymer,  
polyethylene-syn-polypropylene-ethylene/butene copolymer,  
polyethylene-syn-polypropylene-ethylene/hexene copolymer,  
polyethylene-syn-polypropylene-ethylene/octene copolymer,  
polyethylene-syn-polypropylene-ata-polypropylene,
- 20 polyethylene-syn-polypropylene-propylene/butene copolymer,  
polyethylene-syn-polypropylene-propylene/hexene copolymer,  
polyethylene-propylene/butene copolymer-HDPE,  
polyethylene-propylene/butene copolymer-LLDPE,  
polyethylene-propylene/butene copolymer-
- 25 ethylene/propylene copolymer,

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- polyethylene-propylene/butene copolymer-ethylene/butene  
copolymer,  
polyethylene-propylene/butene copolymer-ethylene/hexene  
copolymer,  
5 polyethylene-propylene/butene copolymer-ethylene/octene  
copolymer,  
polyethylene-propylene/butene copolymer-ata-polypropylene,  
polyethylene-propylene/butene copolymer-syn-polypropylene,  
polyethylene-propylene/butene copolymer-propylene/hexene  
10 copolymer,  
polyethylene-propylene/hexene copolymer-HDPE,  
polyethylene-propylene/hexene copolymer-LLDPE,  
polyethylene-propylene/hexene copolymer-  
ethylene/propylene copolymer,  
15 polyethylene-propylene/hexene copolymer-ethylene/butene  
copolymer,  
polyethylene-propylene/hexene copolymer-ethylene/hexene  
copolymer,  
polyethylene-propylene/hexene copolymer-ethylene/octene  
20 copolymer,  
polyethylene-propylene/hexene copolymer-ata-polypropylene,  
polyethylene-propylene/hexene copolymer-syn-polypropylene,  
polyethylene-propylene/hexene copolymer-propylene/butene  
copolymer,  
25 HDPE-polyethylene-LLDPE,

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- HDPE-polyethylene-ethylene/propylene copolymer,  
HDPE-polyethylene-ethylene/butene copolymer,  
HDPE-polyethylene-ethylene/hexene copolymer,  
HDPE-polyethylene-ethylene/octene copolymer,  
5 HDPE-polyethylene-ata-polypropylene,  
HDPE-polyethylene-syn-polypropylene,  
HDPE-polyethylene-propylene/butene copolymer,  
HDPE-polyethylene-propylene/hexene copolymer,  
HDPE-LLDPE-ethylene/propylene copolymer,  
10 HDPE-LLDPE-ethylene/butene copolymer,  
HDPE-LLDPE-ethylene/hexene copolymer,  
HDPE-LLDPE-ethylene/octene copolymer,  
HDPE-LLDPE-ata-polypropylene,  
HDPE-LLDPE-syn-polypropylene,  
15 HDPE-LLDPE-propylene/butene copolymer,  
HDPE-LLDPE-propylene/hexene copolymer,  
HDPE-ethylene/propylene copolymer-LLDPE,  
HDPE-ethylene/propylene copolymer-ethylene/butene  
copolymer,  
20 HDPE-ethylene/propylene copolymer-ethylene/hexene  
copolymer,  
HDPE-ethylene/propylene copolymer-ethylene/octene  
copolymer,  
HDPE-ethylene/propylene copolymer-ata-polypropylene,  
25 HDPE-ethylene/propylene copolymer-syn-polypropylene

HDPE-ethylene/propylene copolymer-propylene/butene  
copolymer,

HDPE-ethylene/propylene copolymer-propylene/hexene  
copolymer,

5 HDPE-ethylene/butene copolymer-LLDPE,

HDPE-ethylene/butene copolymer-ethylene/propylene  
copolymer,

HDPE-ethylene/butene copolymer-ethylene/hexene copolymer,

HDPE-ethylene/butene copolymer-ethylene/octene copolymer,

10 HDPE-ethylene/butene copolymer-ata-polypropylene,

HDPE-ethylene/butene copolymer-syn-polypropylene,

HDPE-ethylene/butene copolymer-propylene/butene copolymer,

HDPE-ethylene/butene copolymer-propylene/hexene copolymer,

HDPE-ethylene/hexene copolymer-LLDPE,

15 HDPE-ethylene/hexene copolymer-ethylene/propylene  
copolymer,

HDPE-ethylene/hexene copolymer-ethylene/butene copolymer,

HDPE-ethylene/hexene copolymer-ethylene/octene copolymer,

HDPE-ethylene/hexene copolymer-ata-polypropylene,

20 HDPE-ethylene/hexene copolymer-syn-polypropylene,

HDPE-ethylene/hexene copolymer-propylene/butene copolymer,

HDPE-ethylene/hexene copolymer-propylene/hexene copolymer,

HDPE-ethylene/octene copolymer-LLDPE,

HDPE-ethylene/octene copolymer-ethylene/propylene

25 copolymer,

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- HDPE-ethylene/octene copolymer-ethylene/butene copolymer,  
HDPE-ethylene/octene copolymer-ethylene/hexene copolymer,  
HDPE-ethylene/octene copolymer-ata-polypropylene,  
HDPE-ethylene/octene copolymer-syn-polypropylene,  
5 HDPE-ethylene/octene copolymer-propylene/butene copolymer,  
HDPE-ethylene/octene copolymer-propylene/hexene copolymer,  
HDPE-ata-polypropylene-LLDPE,  
HDPE-ata-polypropylene-ethylene/propylene copolymer,  
HDPE-ata-polypropylene-ethylene/butene copolymer,  
10 HDPE-ata-polypropylene-ethylene/hexene copolymer,  
HDPE-ata-polypropylene-ethylene/octene copolymer,  
HDPE-ata-polypropylene-syn-polypropylene,  
HDPE-ata-polypropylene-propylene/butene copolymer,  
HDPE-ata-polypropylene-propylene/hexene copolymer,  
15 HDPE-syn-polypropylene-LLDPE,  
HDPE-syn-polypropylene-ethylene/propylene copolymer,  
HDPE-syn-polypropylene-ethylene/butene copolymer,  
HDPE-syn-polypropylene-ethylene/hexene copolymer,  
HDPE-syn-polypropylene-ethylene/octene copolymer,  
20 HDPE-syn-polypropylene-ata-polypropylene,  
HDPE-syn-polypropylene-propylene/butene copolymer,  
HDPE-syn-polypropylene-propylene/hexene copolymer,  
HDPE-propylene/butene copolymer-LLDPE,  
HDPE-propylene/butene copolymer-ethylene/propylene  
25 copolymer,

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- HDPE-propylene/butene copolymer-ethylene/butene copolymer,  
HDPE-propylene/butene copolymer-ethylene/hexene copolymer,  
HDPE-propylene/butene copolymer-ethylene/octene copolymer,  
HDPE-propylene/butene copolymer-ata-polypropylene,  
5 HDPE-propylene/butene copolymer-syn-polypropylene,  
HDPE-propylene/butene copolymer-propylene/hexene  
copolymer,  
HDPE-propylene/hexene copolymer-LLDPE,  
HDPE-propylene/hexene copolymer-ethylene/propylene  
10 copolymer,  
HDPE-propylene/hexene copolymer-ethylene/butene copolymer,  
HDPE-propylene/hexene copolymer-ethylene/hexene copolymer,  
HDPE-propylene/hexene copolymer-ethylene/octene copolymer,  
HDPE-propylene/hexene copolymer-ata-polypropylene,  
15 HDPE-propylene/hexene copolymer-syn-polypropylene,  
HDPE-propylene/hexene copolymer-propylene/butene  
copolymer,  
LLDPE-polyethylene-ethylene/propylene copolymer,  
LLDPE-polyethylene-ethylene/butene copolymer,  
20 LLDPE-polyethylene-ethylene/hexene copolymer,  
LLDPE-polyethylene-ethylene/octene copolymer,  
LLDPE-polyethylene-ata-polypropylene,  
LLDPE-polyethylene-syn-polypropylene,  
LLDPE-polyethylene-propylene/butene copolymer,  
25 LLDPE-polyethylene-propylene/hexene copolymer,

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- LLDPE-HDPE-ethylene/propylene copolymer,  
LLDPE-HDPE-ethylene/butene copolymer,  
LLDPE-HDPE-ethylene/hexene copolymer,  
LLDPE-HDPE-ethylene/octene copolymer,
- 5 LLDPE-HDPE-ata-polypropylene,  
LLDPE-HDPE-syn-polypropylene,  
LLDPE-HDPE-propylene/butene copolymer,  
LLDPE-HDPE-propylene/hexene copolymer,  
LLDPE-ethylene/propylene copolymer-ethylene/butene
- 10 copolymer,  
LLDPE-ethylene/propylene copolymer-ethylene/hexene  
copolymer,  
LLDPE-ethylene/propylene copolymer-ethylene/octene  
copolymer,
- 15 LLDPE-ethylene/propylene copolymer-ata-polypropylene,  
LLDPE-ethylene/propylene copolymer-syn-polypropylene,  
LLDPE-ethylene/propylene copolymer-propylene/butene  
copolymer,  
LLDPE-ethylene/propylene copolymer-propylene/hexene
- 20 copolymer,  
LLDPE-ethylene/butene copolymer-ethylene/propylene  
copolymer,  
LLDPE-ethylene/butene copolymer-ethylene/hexene copolymer,  
LLDPE-ethylene/butene copolymer-ethylene/octene copolymer,
- 25 LLDPE-ethylene/butene copolymer-ata-polypropylene,

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25 copolymer,

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LLDPE-ata-polypropylene-ethylene/butene copolymer,

LLDPE-ata-polypropylene-ethylene/octene copolymer,

5 LLDPE-ata-polypropylene-syn-polypropylene,

LLDPE-ata-polypropylene-propylene hexene copolymer,

LLDPE-syn-polypropylene-ethylene/butene copolymer,

**10** LLDPE-syn-polypropylene-ethylene/hexene copolymer,

LLDPE-syn-polypropylene-ata-polypropylene,

LLDPE-syn-polypropylene-propylene hexene copolymer,

15 LLDPE-propylene/butene copolymer-ethylene/propylene  
copolymer,

LLDPE-propylene/butene copolymer-ethylene/butene  
copolymer,

copolymer,

LLDPE-propylene/butene copolymer-ethylene/octene  
copolymer,

LLDPE-propylene/butene copolymer-syn-polypropylene,

25 LLDPE-propylene/butene copolymer-propylene hexene

- copolymer,  
LLDPE-propylene/hexene copolymer-ethylene/propylene  
copolymer,  
LLDPE-propylene/hexene copolymer-ethylene/butene  
5 copolymer,  
LLDPE-propylene/hexene copolymer-ethylene/hexene  
copolymer,  
LLDPE-propylene/hexene copolymer-ethylene/octene  
copolymer,  
10 LLDPE-propylene/hexene copolymer-ata-polypropylene,  
LLDPE-propylene/hexene copolymer-syn-polypropylene,  
LLDPE-propylene/hexene copolymer-propylene butene  
copolymer,  
ethylene/butene copolymer-polyethylene-ethylene/hexene  
15 copolymer,  
ethylene/butene copolymer-polyethylene-ethylene/octene  
copolymer,  
ethylene/butene copolymer-polyethylene-ata-polypropylene,  
ethylene/butene copolymer-polyethylene-syn-polypropylene,  
20 ethylene/butene copolymer-polyethylene-propylene/butene  
copolymer,  
ethylene/butene copolymer-polyethylene-propylene/hexene  
copolymer,  
ethylene/butene copolymer-HDPE-ethylene/hexene copolymer,  
25 ethylene/butene copolymer-HDPE-ethylene/octene copolymer,

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25 ethylene/butene copolymer-ethylene/hexene copolymer-

- ethylene/octene copolymer,  
ethylene/butene copolymer-ethylene/hexene copolymer-ata-  
polypropylene,  
ethylene/butene copolymer-ethylene/hexene copolymer-syn-  
5 polypropylene,  
ethylene/butene copolymer-ethylene/hexene copolymer-  
propylene/butene copolymer,  
ethylene/butene copolymer-ethylene/hexene copolymer-  
propylene/hexene copolymer,  
10 ethylene/butene copolymer-ethylene/octene copolymer-  
ethylene/hexene copolymer,  
ethylene/butene copolymer-ethylene/octene copolymer-ata-  
polypropylene,  
ethylene/butene copolymer-ethylene/octene copolymer-syn-  
15 polypropylene,  
ethylene/butene copolymer-ethylene/octene copolymer-  
propylene/butene copolymer,  
ethylene/butene copolymer-ethylene/octene copolymer-  
propylene/hexene copolymer,  
20 ethylene/butene copolymer-ata-polypropylene-  
ethylene/hexene copolymer,  
ethylene/butene copolymer-ata-polypropylene-  
ethylene/octene copolymer,  
ethylene/butene copolymer-ata-polypropylene-syn-  
25 polypropylene,

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- ethylene/butene copolymer-ata-polypropylene-  
propylene/butene copolymer,  
ethylene/butene copolymer-ata-polypropylene-  
propylene/hexene copolymer,
- 5   ethylene/butene copolymer-syn-polypropylene-  
ethylene/hexene copolymer,  
ethylene/butene copolymer-syn-polypropylene-  
ethylene/octene copolymer,  
ethylene/butene copolymer-syn-polypropylene-ata-
- 10   polypropylene,  
ethylene/butene copolymer-syn-polypropylene-  
propylene/butene copolymer,  
ethylene/butene copolymer-syn-polypropylene-  
propylene/hexene copolymer,
- 15   ethylene/butene copolymer-propylene/butene copolymer-  
ethylene/hexene copolymer,  
ethylene/butene copolymer-propylene/butene copolymer-  
ethylene/octene copolymer,  
ethylene/butene copolymer-propylene/butene copolymer-ata-
- 20   polypropylene,  
ethylene/butene copolymer-propylene/butene copolymer-syn-  
polypropylene,  
ethylene/butene copolymer-propylene/butene copolymer-  
propylene/hexene copolymer,
- 25   ethylene/butene copolymer-propylene/hexene copolymer-

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- ethylene/hexene copolymer,  
ethylene/butene copolymer-propylene/hexene copolymer-  
ethylene/octene copolymer,  
ethylene/butene copolymer-propylene/hexene copolymer-ata-  
5 polypropylene,  
ethylene/butene copolymer-propylene/hexene copolymer-syn-  
polypropylene,  
ethylene/butene copolymer-propylene/hexene copolymer-  
propylene/butene copolymer,  
10  
ethylene/hexene copolymer-polyethylene-ethylene/octene  
copolymer,  
ethylene/hexene copolymer-polyethylene-ata-polypropylene,  
ethylene/hexene copolymer-polyethylene-syn-polypropylene,  
15  
ethylene/hexene copolymer-polyethylene-propylene/butene  
copolymer,  
ethylene/hexene copolymer-polyethylene-propylene/hexene  
copolymer,  
ethylene/hexene copolymer-HDPE-ethylene/octene copolymer,  
20  
ethylene/hexene copolymer-HDPE-ata-polypropylene,  
ethylene/hexene copolymer-HDPE-syn-polypropylene,  
ethylene/hexene copolymer-HDPE-propylene/butene copolymer,  
ethylene/hexene copolymer-HDPE-propylene/hexene copolymer,  
ethylene/hexene copolymer-LLDPE-ethylene/octene copolymer,  
25  
ethylene/hexene copolymer-LLDPE-ata-polypropylene,

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- ethylene/hexene copolymer-LLDPE-syn-polypropylene,  
ethylene/hexene copolymer-LLDPE-propylene/butene  
copolymer,  
ethylene/hexene copolymer-LLDPE-propylene/hexene  
5 copolymer,  
ethylene/hexene copolymer-ethylene/propylene copolymer-  
ethylene/octene copolymer,  
ethylene/hexene copolymer-ethylene/propylene copolymer-  
ata-polypropylene,  
10 ethylene/hexene copolymer-ethylene/propylene copolymer-  
syn-polypropylene,  
ethylene/hexene copolymer-ethylene/propylene copolymer-  
propylene/butene copolymer,  
ethylene/hexene copolymer-ethylene/propylene copolymer-  
15 propylene/hexene copolymer,  
ethylene/hexene copolymer-ethylene/butene copolymer-  
ethylene/octene copolymer,  
ethylene/hexene copolymer-ethylene/butene copolymer-ata-  
polypropylene,  
20 ethylene/hexene copolymer-ethylene/butene copolymer-syn-  
polypropylene,  
ethylene/hexene copolymer-ethylene/butene copolymer-  
propylene/butene copolymer,  
ethylene/hexene copolymer-ethylene/butene copolymer-  
25 propylene/hexene copolymer,

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ethylene/hexene copolymer-ethylene/octene copolymer-ata-  
polypropylene,

ethylene/hexene copolymer-ethylene/octene copolymer-syn-  
polypropylene,

5 ethylene/hexene copolymer-ethylene/octene copolymer-  
propylene/butene copolymer,

ethylene/hexene copolymer-ethylene/octene copolymer-  
propylene/hexene copolymer,

ethylene/hexene copolymer-ata-polypropylene-

10 ethylene/octene copolymer,

ethylene/hexene copolymer-ata-polypropylene-syn-  
polypropylene,

ethylene/hexene copolymer-ata-polypropylene-  
propylene/butene copolymer,

15 ethylene/hexene copolymer-ata-polypropylene-  
propylene/hexene copolymer,

ethylene/hexene copolymer-syn-polypropylene-  
ethylene/octene copolymer,

ethylene/hexene copolymer-syn-polypropylene-ata-

20 polypropylene,

ethylene/hexene copolymer-syn-polypropylene-  
propylene/butene copolymer,

ethylene/hexene copolymer-syn-polypropylene-  
propylene/hexene copolymer,

25 ethylene/hexene copolymer-polypropylene/butene copolymer-

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- ethylene/octene copolymer,  
ethylene/hexene copolymer-polypropylene/butene copolymer-  
ata-polypropylene,  
ethylene/hexene copolymer-polypropylene/butene copolymer-  
5 syn-polypropylene,  
ethylene/hexene copolymer-polypropylene/butene copolymer-  
propylene/hexene copolymer,  
ethylene/hexene copolymer-polypropylene/hexene copolymer-  
ethylene/octene copolymer,  
10 ethylene/hexene copolymer-polypropylene/hexene copolymer-  
ata-polypropylene,  
ethylene/hexene copolymer-polypropylene/hexene copolymer-  
syn-polypropylene,  
ethylene/hexene copolymer-polypropylene/hexene copolymer-  
15 propylene/butene copolymer,  
ethylene/octene copolymer-polyethylene-ata-polypropylene,  
ethylene/octene copolymer-polyethylene-syn-polypropylene,  
ethylene/octene copolymer-polyethylene-propylene/butene  
copolymer,  
20 ethylene/octene copolymer-polyethylene-propylene/hexene  
copolymer,  
ethylene/octene copolymer-HDPE-ata-polypropylene,  
ethylene/octene copolymer-HDPE-syn-polypropylene,  
ethylene/octene copolymer-HDPE-propylene/butene copolymer,  
25 ethylene/octene copolymer-HDPE-propylene/hexene copolymer,

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ethylene/octene copolymer-LLDPE-ata-polypropylene,  
ethylene/octene copolymer-LLDPE-syn-polypropylene,  
ethylene/octene copolymer-LLDPE-propylene/butene  
copolymer,

- 5 ethylene/octene copolymer-LLDPE-propylene/hexene  
copolymer,

ethylene/octene copolymer-ethylene/propylene copolymer-  
ata-polypropylene,

- 10 ethylene/octene copolymer-ethylene/propylene copolymer-  
syn-polypropylene,

ethylene/octene copolymer-ethylene/propylene copolymer-  
propylene/butene copolymer,

ethylene/octene copolymer-ethylene/propylene copolymer-  
propylene/hexene copolymer,

- 15 ethylene/octene copolymer-ethylene/butene copolymer-ata-  
polypropylene,

ethylene/octene copolymer-ethylene/butene copolymer-syn-  
polypropylene,

ethylene/octene copolymer-ethylene/butene copolymer-

- 20 propylene/butene copolymer,

ethylene/octene copolymer-ethylene/butene copolymer-  
propylene/hexene copolymer,

ethylene/octene copolymer-ethylene/hexene copolymer-ata-  
polypropylene,

- 25 ethylene/octene copolymer-ethylene/hexene copolymer-syn-

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- polypropylene,  
ethylene/octene copolymer-ethylene/hexene copolymer-  
propylene/butene copolymer,  
ethylene/octene copolymer-ethylene/hexene copolymer-  
5 propylene/hexene copolymer,  
ethylene/octene copolymer-ata-polypropylene-syn-  
polypropylene,  
ethylene/octene copolymer-ata-polypropylene-  
propylene/butene copolymer,  
10 ethylene/octene copolymer-ata-polypropylene-  
propylene/hexene copolymer,  
ethylene/octene copolymer-syn-polypropylene-ata-  
polypropylene,  
ethylene/octene copolymer-syn-polypropylene-  
15 propylene/butene copolymer,  
ethylene/octene copolymer-syn-polypropylene-  
propylene/hexene copolymer,  
ethylene/octene copolymer-propylene/butene copolymer-ata-  
polypropylene,  
20 ethylene/octene copolymer-propylene/butene copolymer-syn-  
polypropylene,  
ethylene/octene copolymer-propylene/butene copolymer-  
propylene/hexene copolymer,  
ethylene/octene copolymer-propylene/hexene copolymer-ata-  
25 polypropylene,

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ethylene/octene copolymer-propylene/hexene copolymer-syn-  
polypropylene,

ethylene/octene copolymer-propylene/hexene copolymer-  
propylene/butene copolymer,

5

ata-polypropylene-polyethylene-syn-polypropylene,

ata-polypropylene-polyethylene-propylene/butene copolymer,

ata-polypropylene-polyethylene-propylene/hexene copolymer,

ata-polypropylene-HDPE-syn-polypropylene,

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ata-polypropylene-HDPE-propylene/butene copolymer,

ata-polypropylene-HDPE-propylene/hexene copolymer,

ata-polypropylene-ethylene/octene copolymer-syn-  
polypropylene,

ata-polypropylene-ethylene/octene copolymer-

15

propylene/butene copolymer,

ata-polypropylene-ethylene/octene copolymer-

propylene/hexene copolymer,

ata-polypropylene-ethylene/propylene copolymer-syn-  
polypropylene,

20

ata-polypropylene-ethylene/propylene copolymer-

propylene/butene copolymer,

ata-polypropylene-ethylene/propylene copolymer-  
propylene/hexene copolymer,

ata-polypropylene-ethylene/butene copolymer-syn-

25

polypropylene,

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- ata-polypropylene-ethylene/butene copolymer-  
propylene/butene copolymer,  
ata-polypropylene-ethylene/butene copolymer-  
propylene/hexene copolymer,  
5 ata-polypropylene-ethylene/hexene copolymer-syn-  
polypropylene,  
ata-polypropylene-ethylene/hexene copolymer-  
propylene/butene copolymer,  
ata-polypropylene-ethylene/hexene copolymer-  
10 propylene/hexene copolymer,  
ata-polypropylene-ethylene/octene copolymer-syn-  
polypropylene,  
ata-polypropylene-ethylene/octene copolymer-  
propylene/butene copolymer,  
15 ata-polypropylene-ethylene/octene copolymer-  
propylene/hexene copolymer,  
ata-polypropylene-syn-polypropylene-propylene/butene  
copolymer,  
ata-polypropylene-syn-polypropylene-propylene/hexene  
20 copolymer,  
ata-polypropylene-propylene/butene copolymer-syn-  
polypropylene,  
ata-polypropylene-propylene/butene copolymer-  
propylene/hexene copolymer,  
25 ata-polypropylene-propylene/hexene copolymer-syn-

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- polypropylene,  
ata-polypropylene-propylene/hexene copolymer-  
propylene/butene copolymer,  
syn-polypropylene-polyethylene-propylene/butene copolymer,  
5 syn-polypropylene-polyethylene-propylene/hexene copolymer,  
syn-polypropylene-HDPE-propylene/butene copolymer,  
syn-polypropylene-HDPE-propylene/hexene copolymer,  
syn-polypropylene-LLDPE-propylene/butene copolymer,  
syn-polypropylene-LLDPE-propylene/hexene copolymer,  
10 syn-polypropylene-ethylene/propylene copolymer-  
propylene/butene copolymer,  
syn-polypropylene-ethylene/propylene copolymer-  
propylene/hexene copolymer,  
syn-polypropylene-ethylene/butene copolymer-  
15 propylene/butene copolymer,  
syn-polypropylene-ethylene/butene copolymer-  
propylene/hexene copolymer,  
syn-polypropylene-ethylene/hexene copolymer-  
propylene/butene copolymer,  
20 syn-polypropylene-ethylene/hexene copolymer-  
propylene/hexene copolymer,  
syn-polypropylene-ethylene/octene copolymer-  
propylene/butene copolymer,  
syn-polypropylene-ethylene/octene copolymer-  
25 propylene/hexene copolymer,

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- syn-polypropylene-ata-polypropylene-propylene/butene  
copolymer,
- syn-polypropylene-ata-polypropylene-propylene/hexene  
copolymer,
- 5 syn-polypropylene-propylene/butene copolymer-  
propylene/hexene copolymer,
- syn-polypropylene-propylene/hexene copolymer-  
propylene/butene copolymer,
- propylene/butene copolymer-polyethylene-propylene/hexene
- 10 copolymer,
- propylene/butene copolymer-HDPE-propylene/hexene  
copolymer,
- propylene/butene copolymer-LLDPE-propylene/hexene  
copolymer,
- 15 propylene/butene copolymer-ethylene/propylene copolymer-  
propylene/hexene copolymer,
- propylene/butene copolymer-ethylene/butene copolymer-  
propylene/hexene copolymer,
- propylene/butene copolymer-ethylene/hexene copolymer-
- 20 propylene/hexene copolymer,
- propylene/butene copolymer-ethylene/octene copolymer-  
propylene/hexene copolymer,
- propylene/butene copolymer-ata-polypropylene-  
propylene/hexene copolymer, and
- 25 propylene/butene copolymer-syn-polypropylene-

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propylene/hexene copolymer.

Of these block copolymers, particularly preferable are

polyethylene-polypropylene,

- 5 polyethylene-ethylene/propylene copolymer,  
polyethylene-ethylene/propylene copolymer-polypropylene,  
polyethylene-ethylene/propylene copolymer-LLDPE,  
polyethylene-ethylene/butene copolymer,  
polyethylene-ethylene/butene copolymer-LLDPE,  
10 polypropylene-ethylene/propylene copolymer, and  
polyethylene-LLDPE-HDPE, polyethylene-LLDPE.

- The olefin block copolymer of the invention may be bonded to other structural parts within limits not detrimental to the objects of the invention, with the  
15 proviso that it has the above structure. The polymer of the invention may be a graft modified polymer.

- The olefin copolymer can be favorably used for various molding materials for films, sheets and blow molded products, various additives such as  
20 compatibilizing agent and modifier, coating materials and adhesives. The use application will be described later.

The process for preparing the olefin block copolymer of the invention will be described later.

- The olefin block copolymer of the invention may have  
25 a functional group at the terminal of the main chain.

Examples of the functional groups include the same groups as previously described.

The olefin block copolymer having a functional group at the terminal of the main chain can be favorably used for various additives such as compatibilizing agent and modifier, coating materials and adhesives. The use application will be described later.

The process for preparing the olefin block copolymer having a functional group at the terminal of the main chain will be described later.

Next, the process for preparing an olefin polymer according to the invention is described.

The process for preparing an olefin polymer according to the invention uses an olefin polymerization catalyst comprising the below-described transition metal compound (A), preferably an olefin polymerization catalyst comprising:

(A) the below-described transition metal compound,  
and

20 (B) at least one compound selected from:

(B-1) an organometallic compound,

(B-2) an organoaluminum oxy-compound, and

(B-3) a compound which reacts with the transition metal compound (A) to form an ion pair.

First, the components for forming the olefin polymerization catalyst used in the invention are described.

(A) Transition metal compound

- 5       The transition metal compound (A) for use in the invention is a compound which is represented by the following formula (I) and has properties that, in a  $\beta$ -agostic structure of a cationic complex wherein X in the formula (I) is replaced with a n-propyl group, said
- 10       structure being measured by a density functional method, the distance (r value) between the heteroatom (Z), which has no direct bond to the central metal M and is nearest to the central metal M, and hydrogen at the  $\beta$ -position is not more than 3.0 Å and the electrostatic energy is not
- 15       more than 10 kJ/mol.

The "density functional method" means calculation using a program ADF2000.01 (developed by SCM Co.

- (Netherlands), obtained by making a license contract with SCM Co. and then downloading the program from the home
- 20       page ([html://www.scm.com](http://www.scm.com)) of SCM Co.) and using BLYP method. As the basis function, a Slater type orbital function is used. As for the structure, a function of Triple zeta type is used for the central metal, and a function of Double zeta type is used for other atoms,
- 25       however, in the electrostatic energy evaluation, a

function of Double Zeta type added with a polarization function is used for other atoms. The basis function is used also for the single-point calculation of the optimum structure obtained by structural calculation. In

5 calculations other than the structural calculation, corrections of Pauli's relativistic potentials are made. The "electrostatic energy" means an electrostatic energy between hydrogen at the  $\beta$ -position and the nearest heteroatom. More specifically, the electrostatic energy

10 is an interatomic electrostatic interaction based on the electronic state obtained by assigning electrons obtained by the complex calculation to those two atoms. The electron referred to herein is each electron population of s, p, d orbitals of the two atoms obtained by the

15 complex calculation (single-point calculation in the  $\beta$ -agostic optimum structure obtained after the structural calculation).



In the formula (I), M is a transition metal atom

20 selected from Group 3 to Group 11 of the periodic table, preferably a transition metal atom selected from Group 4 to Group 5, more preferably a transition metal atom of Group 4, specifically titanium, zirconium or hafnium, particularly preferably titanium.

25 m is an integer of 1 to 6.

L is a ligand coordinated to the central metal M and is an organic or inorganic ligand having at least one heteroatom (Z) which has no direct bond to the central metal M.

- 5        Examples of ligand skeletons include cyclopentadienyl skeleton, acetylacetonato skeleton, phenoxy skeleton, amido skeleton, imido skeleton and ligand skeleton which forms the later-described transition metal compound represented by the formula (II-a), (II-b) or (III).
- 10

- The ligand skeleton represented by the formula (II-a) includes ligand skeleton of the formula (II-a) wherein  $R^1$  is a hydrocarbon group and any one of  $R^3$  and  $R^4$  has the later-described heteroatom or heteroatom-containing group, namely, ligand skeleton wherein at least one of  $R^1$ ,  $R^3$  and  $R^4$  has the later-described heteroatom or heteroatom-containing group.
- 15

- The ligand skeleton represented by the formula (II-b) includes ligand skeleton of the formula (II-b) wherein  $R^1$  is a hydrocarbon group and any one of  $R^6$ ,  $R^7$ ,  $R^8$  and  $R^9$  has the later-described heteroatom or heteroatom-containing group, namely, ligand skeleton wherein at least one of  $R^1$ ,  $R^6$ ,  $R^7$ ,  $R^8$  and  $R^9$  has the later-described heteroatom or heteroatom-containing group.
- 20

The ligand skeleton represented by the formula (III) includes ligand skeleton of the formula (III) wherein  $R^{10}$  is a hydrocarbon group and any one of  $R^{11}$ ,  $R^{12}$ ,  $R^{13}$ ,  $R^{14}$  and  $R^{15}$  has the later-described heteroatom or heteroatom-containing group, namely, ligand skeleton wherein at least one of  $R^{11}$ ,  $R^{12}$ ,  $R^{13}$ ,  $R^{14}$  and  $R^{15}$  has the later-described heteroatom or heteroatom-containing group.

The heteroatom is a nonmetal atom other than a carbon atom and a hydrogen atom, and examples thereof include atoms of halogen, nitrogen, oxygen, phosphorus, sulfur and selenium.

$n$  is a number satisfying a valence of  $M$ .

$X$  is an oxygen atom, a hydrogen atom, a halogen atom, a hydrocarbon group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a phosphorus-containing group, a halogen-containing group, a heterocyclic compound residue, a silicon-containing group, a germanium-containing group or a tin-containing group. Plural groups indicated by  $X$  may be bonded to form a ring.

When  $n$  is 2 or greater, plural groups indicated by  $X$  may be the same or different.

Examples of the halogen atoms include fluorine, chlorine, bromine and iodine.





phenylethoxy; acetoxy group; and carbonyl group. When the oxygen-containing group contains carbon atom, the number of carbon atoms is in the range of usually 1 to 30, preferably 1 to 20.

- 5      The sulfur-containing group is, for example, a group containing 1 to 5 sulfur atoms, but the later-described heterocyclic compound residue is not included in this group. Examples of the sulfur-containing groups include sulfonato groups, such as methylsulfonato,
- 10      trifluoromethanesulfonato, phenylsulfonato, benzylsulfonato, p-toluenesulfonato, trimethylbenzenesulfonato, triisobutylbenzenesulfonato, p-chlorobenzenesulfonato and pentafluorobenzenesulfonato; sulfinato groups, such as methylsulfinato,
- 15      phenylsulfinato, benzylsulfinato, p-toluenesulfinato, trimethylbenzenesulfinato and pentafluorobenzenesulfinato; alkylthio groups; and arylthio groups. When the sulfur-containing group contains carbon atom, the number of carbon atoms is in the range of usually 1 to 30,
- 20      preferably 1 to 20.

- The nitrogen-containing group is a group containing 1 to 5 nitrogen atoms, but the later-described heterocyclic compound residue is not included in this group. Examples of the nitrogen-containing groups
- 25      include amino group; alkylamino groups, such as



ethylphosphite and phenylphosphite; phosphonic acid group; and phosphinic acid group.

- Examples of the halogen-containing groups include fluorine-containing groups, such as  $\text{PF}_6$  and  $\text{BF}_4$ ;
- 5 chlorine-containing groups, such as  $\text{ClO}_4$  and  $\text{SbCl}_6$ ; and iodine-containing groups, such as  $\text{IO}_4$ .

- Examples of the heterocyclic compound residues include residues of nitrogen-containing groups such as pyrrole; pyridine, pyrimidine, quinoline and triazine;
- 10 residues of oxygen-containing groups such as furan and pyran; residues of sulfur-containing groups such as thiophene; and groups wherein these heterocyclic compound residues are further substituted with substituents such as alkyl groups of 1 to 30 carbon atoms, preferably 1 to
- 15 20 carbon atoms, or alkoxy groups.

- The silicon-containing group is, for example, a group containing 1 to 5 silicon atoms. Examples of the silicon-containing groups include hydrocarbon-substituted silyl groups, such as phenylsilyl, diphenylsilyl,
- 20 trimethylsilyl, triethylsilyl, tripropylsilyl, tricyclohexylsilyl, triphenylsilyl, methyldiphenylsilyl, tritolylsilyl and trinaphthylsilyl; hydrocarbon-substituted silyl ether groups, such as trimethylsilyl ether; silicon-substituted alkyl groups, such as
- 25 trimethylsilylmethyl; and silicon-substituted aryl groups,

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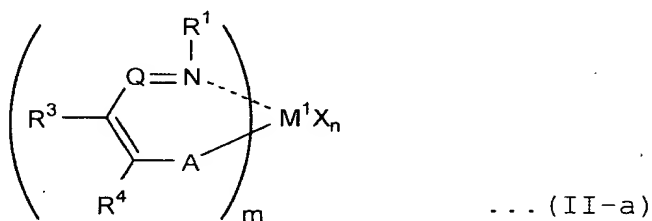
such as trimethylsilylphenyl. When the silicon-containing group contains carbon atom, the number of carbon atoms is in the range of usually 1 to 30, preferably 1 to 20.

- 5        Examples of the germanium-containing groups include groups wherein silicon is replaced with germanium in the above-mentioned silicon-containing groups.

- 10       Examples of the tin-containing groups include groups wherein silicon is replaced with tin in the above-mentioned silicon-containing groups.

As the transition metal compound (A) for use in the invention, a compound represented by the following formula (II-a) or (II-b) is available.

15



- 20       wherein N---M<sup>1</sup> generally means that they are coordinated to each other, but in the present invention they are not always coordinated.

- 25       In the formula (II-a), M<sup>1</sup> is a transition metal atom selected from Group 3 to Group 11 of the periodic table, preferably a transition metal atom of Group 4 to Group 5,

specifically titanium, zirconium, hafnium, vanadium, niobium, tantalum or the like, more preferably a transition metal atom of Group 4, specifically titanium, zirconium or hafnium, still more preferably titanium.

- 5           Q is a nitrogen atom or a carbon atom having a substituent  $R^2$  ( $-C(R^2)=$ ).

A is an oxygen atom, a sulfur atom, a selenium atom or a nitrogen atom having a substituent  $R^5$  ( $-N(R^5)-$ ).

- $R^1$  is a hydrocarbon group having at least one
- 10   heteroatom or a hydrocarbon group having at least one heteroatom-containing group. Examples of the heteroatoms include atoms of halogen, nitrogen, oxygen, phosphorus, sulfur and selenium. The heteroatom-containing group is a group containing a nonmetal atom other than a carbon
- 15   atom and a hydrogen atom, and examples thereof include an oxygen-containing group, a nitrogen-containing group, a sulfur-containing group, a phosphorus-containing group, a halogen atom-containing group and a heterocyclic compound residue. Examples of the oxygen-containing groups, the
- 20   nitrogen-containing groups, the sulfur-containing groups, the phosphorus-containing groups and the heterocyclic compound residues include the same groups as previously described with respect to X in the formula (I). Examples of the halogen-containing groups include groups wherein
- 25   at least one hydrogen is replaced with halogen in the

- hydrocarbon groups of 1 to 30 carbon atoms, preferably 1 to 20 carbon atoms, such as alkyl groups (e.g., methyl, ethyl, propyl, butyl, hexyl, octyl, nonyl, dodecyl and eicosyl), cycloalkyl groups of 3 to 30 carbon atoms (e.g., cyclopentyl, cyclohexyl, norbornyl and adamantyl),
- 5 alkenyl groups (e.g., vinyl, propenyl and cyclohexenyl), arylalkyl groups (e.g., benzyl, phenylethyl and phenylpropyl) and aryl groups (e.g., phenyl, tolyl, dimethylphenyl, trimethylphenyl, ethylphenyl,
- 10 propylphenyl, biphenyl, naphthyl, methylnaphthyl, anthryl and phenanthryl). Specific examples of such groups include trifluoromethyl, perfluoroethyl, pentafluorophenyl, perfluorohexyl, trichloromethyl, perchloroethyl, pentachlorophenyl and perchlorohexyl.
- 15  $R^1$  is preferably a halogen atom-containing hydrocarbon group of 1 to 30 carbon atoms, particularly preferably a fluorine-containing hydrocarbon group of 1 to 30 carbon atoms.
- Specifically,  $R^1$  is trifluoromethyl, perfluoroethyl,
- 20 perfluoropropyl, perfluorobutyl, perfluoropentyl, perfluorohexyl, perfluoroheptyl, perfluorooctyl, perfluorodecyl, 1H,1H-perfluoropropyl, 1H,1H-perfluorobutyl, 1H,1H-perfluoropentyl, 1H,1H-perfluorohexyl, 1H,1H-perfluoroheptyl, 1H,1H-
- 25 perfluorooctyl, 1H,1H-perfluorodecyl, perfluorocyclohexyl,

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trifluoromethylcyclohexyl, bis(trifluoromethyl)cyclohexyl,  
trifluoromethylfluorocyclohexyl, monofluorophenyl,  
difluorophenyl, trifluorophenyl, tetrafluorophenyl,  
pentafluorophenyl, (trifluoromethyl)pentafluorophenyl,  
5 (trifluoromethyl)fluorophenyl, trifluoromethylphenyl,  
bis(trifluoromethyl)phenyl, tris(trifluoromethyl)phenyl,  
tetrakis(trifluoromethyl)phenyl,  
pentakis(trifluoromethyl)phenyl, perfluoroethylphenyl,  
bis(perfluoroethyl)phenyl, perfluoropropylphenyl,  
10 perfluorobutylphenyl, perfluoropentylphenyl,  
perfluorohexylphenyl, bis(perfluorohexyl)phenyl,  
perfluoronaphthyl, perfluorophenanthryl, perfluoroanthryl,  
(trifluoromethyl)tetrafluorophenyl or the like.

$R^2$  to  $R^5$  may be the same or different and are each a  
15 hydrogen atom, a halogen atom, a hydrocarbon group, a  
hydrocarbon-substituted silyl group, an oxygen-containing  
group, a nitrogen-containing group, a sulfur-containing  
group, a boron-containing group, an aluminum-containing  
group, a phosphorus-containing group, a halogen-  
20 containing group, a heterocyclic compound residue, a  
silicon-containing group, a germanium-containing group or  
a tin-containing group. Two or more of  $R^2$  to  $R^5$  may be  
bonded to form a ring.

Examples of the boron-containing groups, the  
25 aluminum-containing groups, the phosphorus-containing

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groups, the halogen-containing groups, the heterocyclic compound residues, the silicon-containing groups, the germanium-containing groups and the tin-containing groups indicated by  $R^2$  to  $R^5$  include the same groups as

- 5 previously described with respect to X in the formula (I)..

Examples of the halogen-containing groups indicated by  $R^2$  to  $R^5$  include the same groups as previously described with respect to  $R^1$  in the formula (II-a).

- Examples of the hydrocarbon groups indicated by  $R^2$
- 10 to  $R^5$  include those of 1 to 30 carbon atoms.
- Specifically, there can be mentioned straight-chain or branched alkyl groups of 1 to 30 carbon atoms, preferably 1 to 20 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl,
- 15 neopentyl and n-hexyl; straight-chain or branched alkenyl groups of 2 to 30 carbon atoms, preferably 2 to 20 carbon atoms, such as vinyl, allyl and isopropenyl; straight-chain or branched alkynyl groups of 2 to 30 carbon atoms, preferably 2 to 20 carbon atom, such as ethynyl and
- 20 propargyl; cyclic saturated hydrocarbon groups of 3 to 30 carbon atoms, preferably 3 to 20 carbon atoms, such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl and adamantyl; cyclic unsaturated hydrocarbon groups of 5 to 30 carbon atoms, such as cyclopentadienyl, indenyl and
- 25 fluorenyl; aryl groups of 6 to 30 carbon atoms,

preferably 6 to 20 carbon atoms, such as phenyl, benzyl, naphthyl, biphenyl, terphenyl, phenanthryl and anthryl; and alkyl-substituted aryl groups, such as tolyl, iso-propylphenyl, t-butylphenyl, dimethylphenyl and di-t-

5 butylphenyl.

The above-mentioned hydrocarbon groups may be substituted with other hydrocarbon groups, and examples of such groups include alkyl groups substituted with aryl groups such as benzyl and cumyl.

10 Examples of the hydrocarbon-substituted silyl groups indicated by  $R^2$  to  $R^5$  include those of 1 to 30 carbon atoms. Specifically, there can be mentioned methylsilyl, dimethylsilyl, trimethylsilyl, ethylsilyl, diethylsilyl, triethylsilyl, diphenylmethylsilyl, triphenylsilyl,

15 dimethylphenylsilyl, dimethyl-t-butylsilyl and dimethyl(pentafluorophenyl)silyl. Of these, preferable are methylsilyl, dimethylsilyl, trimethylsilyl, ethylsilyl, diethylsilyl, triethylsilyl, dimethylphenylsilyl and triphenylsilyl. Particularly

20 preferable are trimethylsilyl, triethylsilyl, triphenylsilyl and dimethylphenylsilyl.

Examples of the oxygen-containing groups indicated by  $R^2$  to  $R^5$  include the same groups as previously described with respect to X in the formula (I).

Examples of the nitrogen-containing groups indicated by  $R^2$  to  $R^5$  include the same groups as previously described with respect to X in the formula (I).

5 Examples of the sulfur-containing groups indicated by  $R^2$  to  $R^5$  include the same groups as previously described with respect to X in the formula (I).

$R^2$  to  $R^5$  are each preferably a hydrogen atom, a halogen atom, a hydrocarbon group, a hydrocarbon-substituted silyl group, an oxygen-containing group, a  
10 nitrogen-containing group, a sulfur-containing group or a halogen-containing group, more preferably a hydrogen atom, a halogen atom, a hydrocarbon group, a hydrocarbon-substituted silyl group or a halogen-containing group.

Examples of the halogen atoms and the halogen-  
15 containing groups indicated by  $R^2$  to  $R^5$  include the same atoms and groups as previously described with respect to  $R^1$  in the formula (II-a).

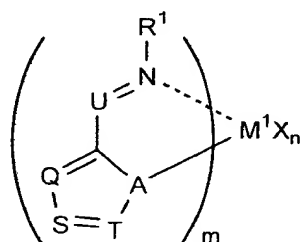
n is a number satisfying a valence of  $M^1$ , specifically an integer of 2 to 4, preferably 2.

20 X is an oxygen atom, a hydrogen atom, a halogen atom, a hydrocarbon group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a phosphorus-containing group, a halogen-containing group,  
25 a heterocyclic compound residue, a silicon-containing

group, a germanium-containing group or a tin-containing group. Examples of such atoms and groups include the same atoms and groups as previously described with respect to X in the formula (I).

- 5        When n is 2 or greater, plural groups indicated by X may be the same or different, and plural groups indicated by X may be bonded to form a ring.

10



... (II-b)

- wherein N---M<sup>1</sup> generally means that they are coordinated  
 15    to each other, but in the present invention they are not always coordinated.

- In the formula (II-b), M<sup>1</sup> is a transition metal atom selected from Group 3 to Group 11 of the periodic table, preferably a transition metal atom of Group 4 to Group 5,  
 20    specifically titanium, zirconium, hafnium, vanadium, niobium, tantalum or the like, more preferably a transition metal atom of Group 4, specifically titanium, zirconium or hafnium, still more preferably titanium.

- m is an integer of 1 to 5, preferably 2 to 4, more  
 25    preferably 2.

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A is a nitrogen atom or a phosphorus atom.

U is a carbon atom having a substituent  $R^6$  ( $-C(R^6)=$ ), a nitrogen atom or a phosphorus atom.

Q is a carbon atom having a substituent  $R^7$  ( $-C(R^7)=$ ),  
5 a nitrogen atom or a phosphorus atom.

S is a carbon atom having a substituent  $R^8$  ( $-C(R^8)=$ ), a nitrogen atom or a phosphorus atom.

T is a carbon atom having a substituent  $R^9$  ( $-C(R^9)=$ ), a nitrogen atom or a phosphorus atom.

10  $R^1$  is a hydrocarbon group having one or more heteroatoms or a hydrocarbon group having one or more heteroatom-containing groups, and has the same meaning as that of  $R^1$  in the formula (II-a).

$R^6$  to  $R^9$  may be the same or different and are each a  
15 hydrogen atom, a halogen atom, a hydrocarbon group, a hydrocarbon-substituted silyl group, an oxygen-containing group, a nitrogen-containing group, a sulfur-containing group, a boron-containing group, an aluminum-containing group, a phosphorus-containing group, a halogen-  
20 containing group, a heterocyclic compound residue, a silicon-containing group, a germanium-containing group or a tin-containing group. Examples of the hydrocarbon groups and the hydrocarbon-substituted silyl groups include the same groups as previously described with  
25 respect to  $R^2$  to  $R^5$  in the formula (II-a). Examples of

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the oxygen-containing groups, the nitrogen-containing groups, the sulfur-containing groups, the nitrogen-containing group, the boron-containing groups, the aluminum-containing groups, the phosphorus-containing groups, the halogen-containing groups, the heterocyclic compound residues, the silicon-containing groups, the germanium-containing groups and the tin-containing groups include the same groups as previously described with respect to X in the formula (I).

- 10  $R^6$  to  $R^9$  are each preferably a hydrogen atom, a halogen atom, a hydrocarbon group, a hydrocarbon-substituted silyl group, an oxygen-containing group, a nitrogen-containing group, a sulfur-containing group or a halogen-containing group, more preferably a hydrogen atom,
- 15 a halogen atom, a hydrocarbon group, a hydrocarbon-substituted silyl group or a halogen-containing group.

- Two or more of  $R^6$  to  $R^9$  may be bonded to form a ring, and when m is 2 or greater,  $R^1$ s,  $R^6$ s,  $R^7$ s,  $R^8$ s and  $R^9$ s may be the same or different, and one group of  $R^6$  to  $R^9$
- 20 contained in one ligand and one group of  $R^6$  to  $R^9$  contained in other ligands may be bonded.

n is a number satisfying a valence of  $M^1$ .

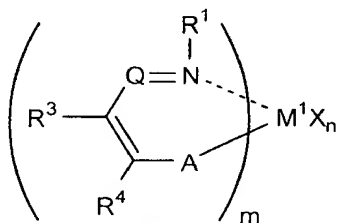
- X is an oxygen atom, a hydrogen atom, a halogen atom, a hydrocarbon group, an oxygen-containing group, a
- 25 sulfur-containing group, a nitrogen-containing group, a

boron-containing group, an aluminum-containing group, a phosphorus-containing group, a halogen-containing group, a heterocyclic compound residue, a silicon-containing group, a germanium-containing group or a tin-containing group. Examples of such atoms and groups include the same atoms and groups as previously described with respect to X in the formula (I).

When n is 2 or greater, plural groups indicated by X may be the same or different, and plural groups indicated by X may be bonded to form a ring.

Similarly to the transition metal compound represented by the formula (I), the transition metal compound (A) represented by the formula (II-a) or (II-b) preferably has properties that the distance between the heteroatom, which has no direct bond to the central metal M and is nearest to the central metal M, and hydrogen at the  $\beta$ -position is not more than 3.0 Å and the electrostatic energy is not more than 10 kJ/mol.

Of the transition metal compounds represented by the formula (II-a) or (II-b), a transition metal compound represented by the following formula (II-a') or (II-b') and having the following structure as R<sup>1</sup> is preferable as the transition metal compound (A) for use in the invention.



...(II-a')

wherein N---M<sup>1</sup> generally means that they are coordinated  
5 to each other, but in the present invention they are not  
always coordinated.

In the formula (II-a'), M<sup>1</sup> is a transition metal  
atom selected from Group 3 to Group 11 of the periodic  
table, preferably a transition metal atom of Group 4 to  
10 Group 5, specifically titanium, zirconium, hafnium,  
vanadium, niobium, tantalum or the like, more preferably  
a transition metal atom of Group 4, specifically titanium,  
zirconium or hafnium, still more preferably titanium.

Q is a nitrogen atom or a carbon atom having a  
15 substituent R<sup>2</sup> (-C(R<sup>2</sup>)=).

A is an oxygen atom, a sulfur atom, a selenium atom  
or a nitrogen atom having a substituent R<sup>5</sup> (-C(R<sup>5</sup>)-).

R<sup>1</sup> is a phenyl group having at least one substituent  
selected from a heteroatom and a heteroatom-containing  
20 groups, an aromatic hydrocarbon group other than a phenyl  
group, an aliphatic hydrocarbon group or an alicyclic  
hydrocarbon group. When R<sup>1</sup> is a phenyl group and the  
position of the carbon atom bonded to a nitrogen atom is  
the 1-position, the phenyl group desirably has, at at  
25 least one position of the 2-position and the 6-position,

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- at least one substituent selected from a heteroatom and a heteroatom-containing group, or has, at the 3-position, the 4-position and the 5-position, at least one substituent selected from a heteroatom other than a
- 5 fluorine atom, a fluorine-containing group containing one carbon atom and not more than two fluorine atoms, a fluorine-containing group containing two or more carbon atoms and a heteroatom-containing group having a heteroatom other than a fluorine atom. When  $R^1$  is an
- 10 aromatic hydrocarbon group other than a phenyl group, an aliphatic hydrocarbon group or an alicyclic hydrocarbon group, this group has one or more substituents selected from heteroatoms and heteroatom-containing groups.

- Examples of the heteroatoms and the heteroatom-
- 15 containing groups indicated by  $R^1$  include the same atoms and groups as previously described with respect to  $R^1$  in the formula (II-a).

- In the transition metal compound represented by the formula (II-a'), when the position of the carbon atom
- 20 bonded to a nitrogen atom is the 1-position,  $R^1$  is preferably a fluorine-containing hydrocarbon group of 1 to 30 carbon atoms which is selected from a phenyl group having, at at least one position of the 2-position and the 6-position, at least one substituent selected from a
- 25 fluorine atom and a fluorine atom-containing group, a

- phenyl group having, at the 3-position, the 4-position and the 5-position, at least one substituent selected from a fluorine-containing group having one carbon atom and not more than two fluorine atoms and a fluorine-
- 5 containing group containing two or more carbon atoms, an aromatic hydrocarbon group other than a phenyl group having at least one substituent selected from a fluorine atom and a fluorine-containing group, an aliphatic hydrocarbon group having at least one substituent
- 10 selected from a fluorine atom and a fluorine-containing group, and an alicyclic hydrocarbon group having at least one substituent selected from a fluorine atom and a fluorine-containing group. Such a transition metal compound is preferable from the viewpoints of activity
- 15 and molecular weight of the resulting polymer.

- Specifically, R<sup>1</sup> is trifluoromethyl, perfluoroethyl, perfluoropropyl, perfluorobutyl, perfluoropentyl, perfluorohexyl, perfluoroheptyl, perfluorooctyl, perfluorodecyl, 1H,1H-perfluoropropyl, 1H,1H-
- 20 perfluorobutyl, 1H,1H-perfluoropentyl, 1H,1H-perfluorohexyl, 1H,1H-perfluoroheptyl, 1H,1H-perfluorooctyl, 1H,1H-perfluorodecyl, perfluorocyclohexyl, trifluoromethylcyclohexyl, bis(trifluoromethyl)cyclohexyl, trifluoromethylfluorocyclohexyl, monofluorophenyl,
- 25 difluorophenyl, trifluorophenyl, tetrafluorophenyl,

- pentafluorophenyl, (trifluoromethyl)pentafluorophenyl,  
(trifluoromethyl)fluorophenyl, trifluoromethylphenyl,  
bit(trifluoromethyl)phenyl, tris(trifluoromethyl)phenyl,  
tetrakis(trifluoromethyl)phenyl,
- 5 pentakis(trifluoromethyl)phenyl, perfluoroethylphenyl,  
bis(perfluoroethyl)phenyl, perfluoropropylphenyl,  
perfluorobutylphenyl, perfluoropentylphenyl,  
perfluorohexylphenyl, bis(perfluorohexyl)phenyl,  
perfluoronaphthyl, perfluorophenanthryl, perfluoroanthryl,
- 10 (trifluoromethyl)tetrafluorophenyl or the like.
- $R^1$  is preferably a fluorine-containing aliphatic  
hydrocarbon group of 3 to 30 carbon atoms, and examples  
thereof include 1H,1H-perfluoropropyl, 1H,1H-  
perfluorobutyl, 1H,1H-perfluoropentyl, 1H,1H-  
15 perfluorohexyl, 1H,1H-perfluoroheptyl, 1H,1H-  
perfluorooctyl and 1H,1H-perfluorodecyl. Also preferable  
are aromatic hydrocarbon groups of 6 to 30 carbon atoms  
substituted with fluorine and/or fluorine-containing  
hydrocarbon, such as monofluorophenyl, difluorophenyl,  
20 trifluorophenyl, tetrafluorophenyl, pentafluorophenyl,  
(trifluoromethyl)pentafluorophenyl,  
(trifluoromethyl)fluorophenyl, trifluoromethylphenyl,  
bis(trifluoromethyl)phenyl, tris(trifluoromethyl)phenyl,  
tetrakis(trifluoromethyl)phenyl,
- 25 pentakis(trifluoromethyl)phenyl, perfluoroethylphenyl,

bis(perfluoroethyl)phenyl, perfluoropropylphenyl,  
perfluorobutylphenyl, perfluoropentylphenyl,  
perfluorohexylphenyl, bis(perfluorohexyl)phenyl,  
perfluoronaphthyl, perfluorophenanthryl, perfluoroanthryl  
5 and (trifluoromethyl)tetrafluorophenyl.

Of the above examples, particularly preferable as  $R^1$   
are monofluorophenyl, difluorophenyl, trifluorophenyl,  
tetrafluorophenyl, pentafluorophenyl,  
(trifluoromethyl)pentafluorophenyl and 1H,1H-  
10 perfluorooctyl.

$R^2$  to  $R^5$  may be the same or different and are each a  
hydrogen atom, a halogen atom, a hydrocarbon group, a  
hydrocarbon-substituted silyl group, an oxygen-containing  
group, a nitrogen-containing group, a sulfur-containing  
15 group, a boron-containing group, an aluminum-containing  
group, a phosphorus-containing group, a halogen-  
containing group, a heterocyclic compound residue, a  
silicon-containing group, a germanium-containing group or  
a tin-containing group. Two or more of  $R^2$  to  $R^5$  may be  
20 bonded to form a ring.

Examples of the boron-containing groups, the  
aluminum-containing groups, the phosphorus-containing  
groups, the halogen-containing groups, the heterocyclic  
compound residues, the silicon-containing groups, the  
25 germanium-containing groups and the tin-containing groups

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indicated by  $R^2$  to  $R^5$  include the same groups as previously described with respect to X in the formula (I).

Examples of the halogen-containing groups indicated by  $R^2$  to  $R^5$  include the same groups as previously described with respect to  $R^1$  in the formula (II-a).

Examples of the hydrocarbon groups indicated by  $R^2$  to  $R^5$  include those of 1 to 30 carbon atoms. Specifically, there can be mentioned straight-chain or branched alkyl groups of 1 to 30 carbon atoms, preferably 1 to 20 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, neopentyl and n-hexyl; straight-chain or branched alkenyl groups of 2 to 30 carbon atoms, preferably 2 to 20 carbon atoms, such as vinyl, allyl and isopropenyl; straight-chain or branched alkynyl groups of 2 to 30 carbon atoms, preferably 2 to 20 carbon atom, such as ethynyl and propargyl; cyclic saturated hydrocarbon groups of 3 to 30 carbon atoms, preferably 3 to 20 carbon atoms, such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl and adamantyl; cyclic unsaturated hydrocarbon groups of 5 to 30 carbon atoms, such as cyclopentadienyl, indenyl and fluorenyl; aryl groups of 6 to 30 carbon atoms, preferably 6 to 20 carbon atoms, such as phenyl, benzyl, naphthyl, biphenyl, terphenyl, phenanthryl and anthryl; and alkyl-substituted aryl groups, such as tolyl,

iso-propylphenyl, t-butylphenyl, dimethylphenyl and di-t-butylphenyl.

The above-mentioned hydrocarbon groups may be substituted with other hydrocarbon groups, and examples  
5 of such groups include alkyl groups substituted with aryl groups such as benzyl and cumyl.

Examples of the hydrocarbon-substituted silyl groups indicated by  $R^2$  to  $R^5$  include those of 1 to 30 carbon atoms. Specifically, there can be mentioned methylsilyl,  
10 dimethylsilyl, trimethylsilyl, ethylsilyl, diethylsilyl, triethylsilyl, diphenylmethylsilyl, triphenylsilyl, dimethylphenylsilyl, dimethyl-t-butylsilyl and dimethyl(pentafluorophenyl)silyl. Of these, preferable are methylsilyl, dimethylsilyl, trimethylsilyl,  
15 ethylsilyl, diethylsilyl, triethylsilyl, dimethylphenylsilyl and triphenylsilyl. Particularly preferable are trimethylsilyl, triethylsilyl, triphenylsilyl and dimethylphenylsilyl.

Examples of the oxygen-containing groups indicated  
20 by  $R^2$  to  $R^5$  include the same groups as previously described with respect to X in the formula (I).

Examples of the nitrogen-containing groups indicated by  $R^2$  to  $R^5$  include the same groups as previously described with respect to X in the formula (I).

Examples of the sulfur-containing groups indicated by  $R^2$  to  $R^5$  include the same groups as previously described with respect to X in the formula (I).

5 Examples of the halogen atoms and the halogen-containing groups indicated by  $R^2$  to  $R^5$  include the same groups as previously described with respect to  $R^1$  in the formula (II-a).

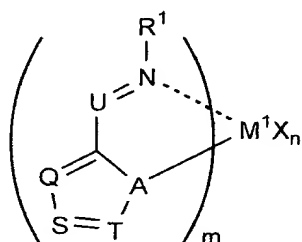
10  $R^2$  to  $R^5$  are each preferably a hydrogen atom, a halogen atom, a hydrocarbon group, a hydrocarbon-substituted silyl group, an oxygen-containing group, a nitrogen-containing group, a sulfur-containing group or a halogen-containing group, more preferably a hydrogen atom, a halogen atom, a hydrocarbon group, a hydrocarbon-substituted silyl group or a halogen-containing group.

15 n is a number satisfying a valence of  $M^1$ , specifically an integer of 2 to 4, preferably 2.

20 X is an oxygen atom, a hydrogen atom, a halogen atom, a hydrocarbon group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a phosphorus-containing group, a halogen-containing group, a heterocyclic compound residue, a silicon-containing group, a germanium-containing group or a tin-containing group. Examples of such atoms and groups include the

same atoms and groups as previously described with respect to X in the formula (I).

When n is 2 or greater, plural groups indicated by X may be the same or different, and plural groups indicated  
5 by X may be bonded to form a ring.



... (II-b')

wherein N---M<sup>1</sup> generally means that they are coordinated to each other, but in the present invention they are not always coordinated.

In the formula (II-b'), M<sup>1</sup> is a transition metal  
15 atom selected from Group 3 to Group 11 of the periodic table, preferably a transition metal atom of Group 4 to Group 5, specifically titanium, zirconium, hafnium, vanadium, niobium, tantalum or the like, more preferably a transition metal atom of Group 4, specifically titanium,  
20 zirconium or hafnium, still more preferably titanium.

m is an integer of 1 to 5, preferably 2 to 4, more preferably 2.

A is a nitrogen atom or a phosphorus atom.

U is a carbon atom having a substituent R<sup>6</sup> (-C(R<sup>6</sup>)=),  
25 a nitrogen atom or a phosphorus atom.



Q is a carbon atom having a substituent  $R^7$  ( $-C(R^7)=$ ), a nitrogen atom or a phosphorus atom.

S is a carbon atom having a substituent  $R^8$  ( $-C(R^8)=$ ), a nitrogen atom or a phosphorus atom.

- 5        T is a carbon atom having a substituent  $R^9$  ( $-C(R^9)=$ ), a nitrogen atom or a phosphorus atom.

$R^1$  is a hydrocarbon group having one or more heteroatoms or a hydrocarbon group having one or more heteroatom-containing groups, and has the same meaning as  
10        that of  $R^1$  in the formula (II-a').

$R^6$  to  $R^9$  may be the same or different and are each a hydrogen atom, a halogen atom, a hydrocarbon group, a hydrocarbon-substituted silyl group, an oxygen-containing group, a nitrogen-containing group, a sulfur-containing  
15        group, a boron-containing group, an aluminum-containing group, a phosphorus-containing group, a halogen-containing group, a heterocyclic compound residue, a silicon-containing group, a germanium-containing group or a tin-containing group. Examples of the hydrocarbon  
20        groups and the hydrocarbon-substituted silyl groups include the same groups as previously described with respect to  $R^2$  to  $R^5$  in the formula (II-a). Examples of the oxygen-containing groups, the nitrogen-containing groups, the sulfur-containing groups, the nitrogen-  
25        containing group, the boron-containing groups, the

aluminum-containing groups, the phosphorus-containing groups, the halogen-containing groups, the heterocyclic compound residues, the silicon-containing groups, the germanium-containing groups and the tin-containing groups  
5 include the same groups as previously described with respect to X in the formula (I).

$R^6$  to  $R^9$  are each preferably a hydrogen atom, a halogen atom, a hydrocarbon group, a hydrocarbon-substituted silyl group, an oxygen-containing group, a  
10 nitrogen-containing group, a sulfur-containing group or a halogen-containing group, more preferably a hydrogen atom, a hydrocarbon group, a hydrocarbon-substituted silyl group, a halogen atom or a halogen-containing group.

Two or more of  $R^6$  to  $R^9$  may be bonded to form a ring,  
15 and when m is 2 or greater,  $R^1$ s,  $R^6$ s,  $R^7$ s,  $R^8$ s and  $R^9$ s may be the same or different, and one group of  $R^6$  to  $R^9$  contained in one ligand and one group of  $R^6$  to  $R^9$  contained in other ligands may be bonded.

n is a number satisfying a valence of  $M^1$ .

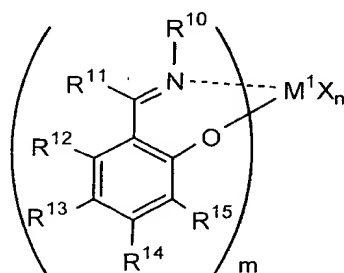
20 X is an oxygen atom, a hydrogen atom, a halogen atom, a hydrocarbon group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a phosphorus-containing group, a halogen-containing group,  
25 a heterocyclic compound residue, a silicon-containing

group, a germanium-containing group or a tin-containing group. Examples of such atoms and groups include the same atoms and groups as previously described with respect to X in the formula (I).

- 5           When n is 2 or greater, plural groups indicated by X may be the same or different, and plural groups indicated by X may be bonded to form a ring.

- 10           As the transition metal compound (A) for use in the invention, there can be also mentioned a transition metal compound represented by the following formula (III) and having properties that, in a  $\beta$ -agostic structure of a cationic complex wherein one of X in the formula (III) is replaced with a n-propyl group, said structure being measured by a density functional method, the distance
- 15           between the heteroatom, which has no direct bond to the central metal M and is nearest to the central metal M, and hydrogen at the  $\beta$ -position is not more than 3.0 Å and the electrostatic energy is not more than 10 kJ/mol.

20



... (III)

wherein N---M<sup>1</sup> generally means that they are coordinated to each other, but in the present invention they are not always coordinated.

In the formula (III), M<sup>1</sup> is a transition metal atom  
5 selected from Group 4 to Group 5 of the periodic table, specifically titanium, zirconium, hafnium, vanadium, niobium, tantalum or the like, preferably a transition metal atom of Group 4, specifically titanium, zirconium or hafnium, more preferably titanium.

10 m is 1 or 2, preferably 2.

R<sup>10</sup> is a hydrocarbon group having at least one heteroatom or a hydrocarbon group having at least one heteroatom-containing group. Examples of the heteroatoms include atoms of halogen, nitrogen, oxygen, phosphorus,  
15 sulfur and selenium. The heteroatom-containing group is a group containing a nonmetal atom other than a carbon atom and a hydrogen atom, and examples thereof include an oxygen-containing group, a nitrogen-containing group, a sulfur-containing group, a phosphorus-containing group, a  
20 halogen atom-containing group and a heterocyclic compound residue. Examples of the oxygen-containing groups, the nitrogen-containing groups, the sulfur-containing groups, the phosphorus-containing groups and the heterocyclic compound residues include the same groups as previously  
25 described with respect to X in the formula (I). Examples

of the halogen-containing groups include groups wherein at least one hydrogen is replaced with halogen in hydrocarbon groups of 1 to 30 carbon atoms, preferably 1 to 20 carbon atoms, such as alkyl groups (e.g., methyl, ethyl, propyl, butyl, hexyl, octyl, nonyl, dodecyl and eicosyl), cycloalkyl groups of 3 to 30 carbon atoms (e.g., cyclopentyl, cyclohexyl, norbornyl and adamantyl), alkenyl groups (e.g., vinyl, propenyl and cyclohexenyl), arylalkyl groups (e.g., benzyl, phenylethyl and phenylpropyl) and aryl groups (e.g., phenyl, tolyl, dimethylphenyl, trimethylphenyl, ethylphenyl, propylphenyl, biphenyl, naphthyl, methylnaphthyl, anthryl and phenanthryl). Specific examples of such groups include trifluoromethyl, perfluoroethyl, pentafluorophenyl, perfluorohexyl, trichloromethyl, perchloroethyl, pentachlorophenyl and perchlorohexyl.

R<sup>10</sup> is preferably a halogen atom-containing hydrocarbon group of 1 to 30 carbon atoms, particularly preferably a fluorine-containing hydrocarbon group of 1 to 30 carbon atoms.

Specifically, R<sup>10</sup> is trifluoromethyl, perfluoroethyl, perfluoropropyl, perfluorobutyl, perfluoropentyl, perfluorohexyl, perfluoroheptyl, perfluorooctyl, perfluorodecyl, 1H,1H-perfluoropropyl, 1H,1H-perfluorobutyl, 1H,1H-perfluoropentyl, 1H,1H-

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- perfluorohexyl, 1H,1H-perfluoroheptyl, 1H,1H-perfluorooctyl, 1H,1H-perfluorodecyl, perfluorocyclohexyl, trifluoromethylcyclohexyl, bis(trifluoromethyl)cyclohexyl, trifluoromethylfluorocyclohexyl, monofluorophenyl,
- 5 difluorophenyl, trifluorophenyl, tetrafluorophenyl, pentafluorophenyl, (trifluoromethyl)pentafluorophenyl, (trifluoromethyl)fluorophenyl, trifluoromethylphenyl, bis(trifluoromethyl)phenyl, tris(trifluoromethyl)phenyl, tetrakis(trifluoromethyl)phenyl,
- 10 pentakis(trifluoromethyl)phenyl, perfluoroethylphenyl, bis(perfluoroethyl)phenyl, perfluoropropylphenyl, perfluorobutylphenyl, perfluoropentylphenyl, perfluorohexylphenyl, bis(perfluorohexyl)phenyl, perfluoronaphthyl, perfluorophenanthryl, perfluoroanthryl,
- 15 (trifluoromethyl)tetrafluorophenyl or the like.

- R<sup>11</sup> to R<sup>14</sup> may be the same or different and are each a hydrogen atom, a halogen atom, a halogen-containing group, a hydrocarbon group, a hydrocarbon-substituted silyl group, an oxygen-containing group, a nitrogen-
- 20 containing group or a sulfur-containing group. Examples of such atoms and groups include the same atoms and groups as previously described with respect to R<sup>2</sup> to R<sup>5</sup> in the formula (II-a).

- R<sup>15</sup> is a halogen atom, a halogen-containing group, a
- 25 hydrocarbon group or a hydrocarbon-substituted silyl

group. Examples of such atoms and groups include the same atoms and groups as previously described with respect to  $R^2$  to  $R^5$  in the formula (II-a).

- Examples of the hydrocarbon groups indicated by  $R^{15}$
- 5 include those of 1 to 30 carbon atoms. Preferred examples thereof include straight-chain or branched alkyl groups of 1 to 30 carbon atoms, preferably 1 to 20 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl,
- 10 neopentyl and n-hexyl; hydrocarbon groups having alicyclic skeleton and having 3 to 30 carbon atoms, preferably 3 to 20 carbon atoms, such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, norbornyl and adamantyl; aryl groups of 6 to 30 carbon atoms,
- 15 preferably 6 to 20 carbon atoms, such as phenyl, benzyl, naphthyl, biphenyl, triphenyl, fluorenyl, anthryl and phenanthryl; and groups wherein these groups are further substituted with an alkyl group of 1 to 30 carbon atoms, preferably 1 to 20 carbon atoms, or an aryl group of 6 to
- 20 30 carbon atoms, preferably 6 to 20 carbon atoms. Of these, tert-butyl is more preferable.

Examples of the hydrocarbon-substituted silyl groups indicated by  $R^{15}$  include the same groups as previously described with respect to  $R^2$  to  $R^5$  in the formula (II-a).

Examples of the heteroatoms and the heteroatom-containing groups indicated by  $R^{15}$  include the same atoms and groups as previously described with respect to  $R^1$  in the formula (II-a).

- 5         $R^{10}$  and  $R^{11}$  to  $R^{15}$  may be the same or different, and two or more of them may be bonded to form a ring.

$n$  is a number satisfying a valence of  $M^1$ , specifically an integer of 2 to 4, preferably 2.

- 10         $X$  is an oxygen atom, a hydrogen atom, a halogen atom, a hydrocarbon group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a phosphorus-containing group, a halogen-containing group, a heterocyclic compound residue, a silicon-containing
- 15        group, a germanium-containing group or a tin-containing group. Examples of such atoms and groups include the same atoms and groups as previously described with respect to  $X$  in the formula (I).

- 20        When  $n$  is 2 or greater, plural groups indicated by  $X$  may be the same or different, and plural groups indicated by  $X$  may be bonded to form a ring.

- As the transition metal compound (A), there can be also mentioned a transition metal compound represented by the following formula (III') and having the following
- 25        structure as  $R^{10}$ .





10            In the above formula,  $M^1$ ,  $m$ ,  $R^{11}$  to  $R^{14}$ ,  $R^{15}$ ,  $n$  and  $X$  have the same meanings as those of  $M^1$ ,  $m$ ,  $R^{11}$  to  $R^{14}$ ,  $R^{15}$ ,  $n$  and  $X$  in the formula (III).

R<sup>10</sup> is a phenyl group having at least one substituent selected from a heteroatom and a heteroatom-containing group, an aromatic hydrocarbon group other than a phenyl group, an aliphatic hydrocarbon group or an alicyclic hydrocarbon group. When R<sup>10</sup> is a phenyl group and the position of the carbon atom bonded to nitrogen is the 1-position, this phenyl group has, at at least one position of the 2-position and the 6-position, one or more substituents selected from a heteroatom and a heteroatom-containing group, or has, at the 3-position, the 4-position and the 5-position, at least one substituent selected from a heteroatom other than a fluorine atom, a fluorine-containing group having one

carbon atom and not more than two fluorine atoms, a fluorine-containing group having two or more carbon atoms, and a heteroatom-containing group having a heteroatom other than a fluorine atom. When  $R^{10}$  is an aromatic hydrocarbon group other than a phenyl group, an aliphatic hydrocarbon group or an alicyclic group, this group has at least one substituent selected from a heteroatom and a heteroatom-containing group.

Examples of the heteroatoms and the heteroatom-containing groups include the same atoms and groups as previously described with respect to  $R^1$  in the formula (II-a).

In the transition metal compound represented by the formula (III), when the position of the carbon atom bonded to a nitrogen atom is the 1-position,  $R^{10}$  is preferably a fluorine-containing hydrocarbon group of 1 to 30 carbon atoms which is selected from a phenyl group having, at at least one position of the 2-position and the 6-position, one or more substituents selected from a heteroatom and a heteroatom-containing group, a phenyl group having, at the 3-position, the 4-position and the 5-position, at least one substituent selected from a fluorine-containing group containing one carbon atom and not more than two fluorine atoms and a fluorine-containing group containing two or more carbon atoms, an

- aromatic hydrocarbon group other than a phenyl group having at least one substituent selected from a fluorine atom and a fluorine-containing group, an aliphatic hydrocarbon group having at least one substituent
- 5 selected from a fluorine atom and a fluorine-containing group, and an alicyclic hydrocarbon group having at least one substituent selected from a fluorine atom and a fluorine-containing group. Such a transition metal compound is preferable from the viewpoints of activity
- 10 and molecular weight of the resulting polymer.

- As for the substitution position of the substituent having a heteroatom or a heteroatom-containing group, when  $R^{10}$  is aromatic, this substituent is preferably present at the position of a carbon atom (carbon atom at
- 15 the  $\beta$ -position) adjacent to the carbon atom in  $R^{10}$  that is bonded to a nitrogen atom, and when  $R^{10}$  is aliphatic, the substituent is preferably present at the adjacent position or its adjacent position ( $\beta$ -position or  $\gamma$ -position).

- 20 Examples of the heteroatoms and the heteroatom-containing groups include the same atoms and groups as previously described. Particularly, fluorine is preferable as the heteroatom, and a fluorine-containing group is preferable as the heteroatom-containing group.

- 25 Examples of  $R^{10}$  include

- trifluoromethyl, perfluoroethyl, perfluoropropyl,  
perfluorobutyl, perfluoropentyl, perfluorohexyl,  
perfluoroheptyl, perfluorooctyl, perfluorodecyl,  
1H,1H-perfluoropropyl, 1H,1H-perfluorobutyl,  
5 1H,1H-perfluoropentyl, 1H,1H-perfluorohexyl,  
1H,1H-perfluoroheptyl, 1H,1H-perfluorooctyl,  
1H,1H-perfluorodecyl, perfluorocyclohexyl,  
trifluoromethylcyclohexyl,  
bis(trifluoromethyl)cyclohexyltrifluoromethylfluorocyclo-  
10 hexyl, monofluorophenyl, difluorophenyl, trifluorophenyl,  
tetrafluorophenyl, pentafluorophenyl,  
(trifluoromethyl)pentafluorophenyl,  
(trifluoromethyl)fluorophenyl, trifluoromethylphenyl,  
bis(trifluoromethyl)phenyl, tris(trifluoromethyl)phenyl,  
15 tetrakis(trifluoromethyl)phenyl,  
pentakis(trifluoromethyl)phenyl, perfluoroethylphenyl,  
bis(perfluoroethyl)phenyl, perfluoropropylphenyl,  
perfluorobutylphenyl, perfluoropentylphenyl,  
perfluorohexylphenyl, bis(perfluorohexyl)phenyl,  
20 perfluoronaphthyl, perfluorophenanthryl,  
perfluoroanthryl and (trifluoromethyl)tetrafluorophenyl.

R<sup>10</sup> is preferably a fluorine-containing aliphatic hydrocarbon group of 3 to 30 carbon atoms. Examples include aliphatic hydrocarbon groups of 3 to 30 carbon  
25 atoms substituted with fluorine and/or fluorine-

containing hydrocarbon such as

- 1H,1H-perfluoropropyl, 1H,1H-perfluorobutyl,  
1H,1H-perfluoropentyl, 1H,1H-perfluorohexyl,  
1H,1H-perfluoroheptyl, 1H,1H-perfluorooctyl,  
5 1H,1H-perfluorodecyl or monofluorophenyl,  
difluorophenyl, trifluorophenyl, tetrafluorophenyl,  
pentafluorophenyl, (trifluoromethyl)pentafluorophenyl,  
(trifluoromethyl)fluorophenyl, trifluoromethylphenyl,  
bis(trifluoromethyl)phenyl, tris(trifluoromethyl)phenyl,  
10 tetrakis(trifluoromethyl)phenyl,  
pentakis(trifluoromethyl)phenyl, perfluoroethylphenyl,  
bis(perfluoroethyl)phenyl, perfluoropropylphenyl,  
perfluorobutylphenyl, perfluoropentylphenyl,  
perfluorohexylphenyl, bis(perfluorohexyl)phenyl,  
15 perfluoronaphthyl, perfluorophenanthryl,  
perfluoroanthryl, and (trifluoromethyl)tetrafluorophenyl.

- $R^{10}$  is particularly preferably an aromatic  
hydrocarbon group of 6 to 30 carbon atoms substituted  
with fluorine, an aromatic hydrocarbon group of 8 to 30  
20 carbon atoms substituted with a fluorine-containing  
hydrocarbon of 2 or more carbon atoms or an aromatic  
hydrocarbon group of 7 to 30 carbon atoms substituted  
with fluorine and a fluorine-containing hydrocarbon group.  
Examples include  
25 monofluorophenyl, difluorophenyl, trifluorophenyl,

- tetrafluorophenyl, pentafluorophenyl,  
(trifluoromethyl)pentafluorophenyl,  
(trifluoromethyl)fluorophenyl, trifluoromethylphenyl,  
tris(trifluoromethyl)phenyl,  
5 tetrakis(trifluoromethyl)phenyl,  
pentakis(trifluoromethyl)phenyl, perfluoroethylphenyl,  
bis(perfluoroethyl)phenyl, perfluoropropylphenyl,  
perfluorobutylphenyl, perfluoropentylphenyl,  
perfluorohexylphenyl, bis(perfluorohexyl)phenyl,  
10 perfluoronaphthyl, perfluorophenanthryl,  
perfluoroanthryl and (trifluoromethyl)tetrafluorophenyl.

- Of these, particularly preferable as  $R^{10}$  are  
2-fluorophenyl group, 2,6-difluorophenyl group,  
2,4,6-trifluorophenyl group, pentafluorophenyl group,  
15 4-trifluoromethyl 2,3,5,6-tetrafluorophenyl group,  
2-trifluoromethylphenyl group and 1H,1H-perfluorooctyl  
group.

- As for the substitution position of fluorine, when  
 $R^{10}$  is aromatic, this fluorine is preferably present at  
20 the position of a carbon atom (carbon atom at the  $\beta$ -  
position) adjacent to the carbon atom in  $R^{10}$  that is  
bonded to a nitrogen atom, and when  $R^{10}$  is aliphatic, the  
fluorine is preferably present at the adjacent position  
or its adjacent position ( $\beta$ -position or  $\gamma$ -position).

R<sup>11</sup> to R<sup>14</sup> may be the same or different and are each a hydrogen atom, a halogen atom, a halogen-containing group, a hydrocarbon group, a hydrocarbon-substituted silyl group, an oxygen-containing group, a nitrogen-containing group or a sulfur-containing group. Examples of such atoms and groups include the same atoms and groups as previously described with respect to R<sup>2</sup> to R<sup>5</sup> in the formula (II-a).

R<sup>15</sup> is a halogen atom, a halogen-containing group, a hydrocarbon group or a hydrocarbon-substituted silyl group. Examples of such atoms and groups include the same atoms and groups as previously described with respect to R<sup>2</sup> to R<sup>5</sup> in the formula (II-a).

Examples of the hydrocarbon groups indicated by R<sup>15</sup> include those of 1 to 30 carbon atoms. Preferred examples thereof include straight-chain or branched alkyl groups of 1 to 30 carbon atoms, preferably 1 to 20 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, neopentyl and n-hexyl; hydrocarbon groups having alicyclic skeleton and having 3 to 30 carbon atoms, preferably 3 to 20 carbon atoms, such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, norbornyl and adamantyl; aryl groups of 6 to 30 carbon atoms, preferably 6 to 20 carbon atoms, such as phenyl, benzyl,

naphthyl, biphenyl, triphenyl, fluorenyl, anthryl and phenanthryl; and groups wherein these groups are further substituted with an alkyl group of 1 to 30 carbon atoms, preferably 1 to 20 carbon atoms, or an aryl group of 6 to 30 carbon atoms, preferably 6 to 20 carbon atoms. Of these, tert-butyl is more preferable.

Examples of the hydrocarbon-substituted silyl groups indicated by  $R^{15}$  include the same groups as previously described with respect to  $R^2$  to  $R^5$  in the formula (II-a).

10 Examples of the halogen atoms and the halogen-containing groups indicated by  $R^{15}$  include the same atoms and groups as previously described with respect to  $R^1$  in the formula (II-a).

$R^{10}$  and  $R^{11}$  to  $R^{15}$  may be the same or different, and 15 two or more of them may be bonded to form a ring.

$n$  is a number satisfying a valence of  $M^1$ , specifically an integer of 2 to 4, preferably 2.

$X$  is an oxygen atom, a hydrogen atom, a halogen atom, a hydrocarbon group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, a boron-containing group, an aluminum-containing group, a phosphorus-containing group, a halogen-containing group, a heterocyclic compound residue, a silicon-containing group, a germanium-containing group or a tin-containing 20 group. Examples of such atoms and groups include the 25

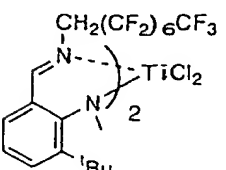
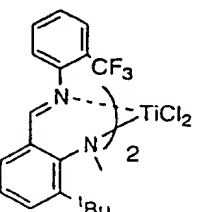
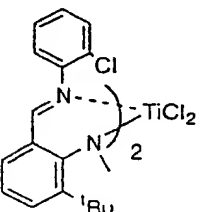
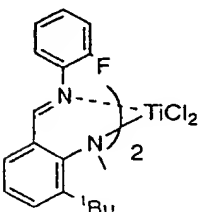
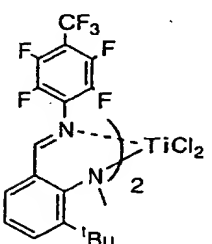
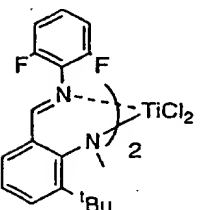
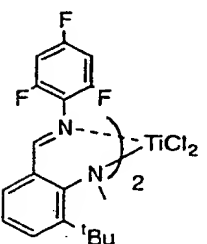
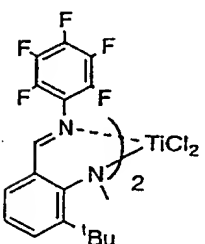
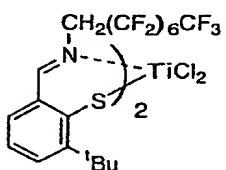
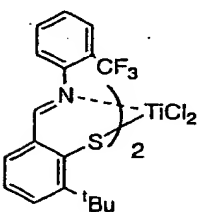
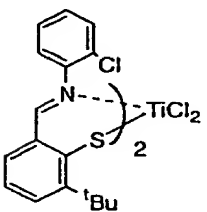
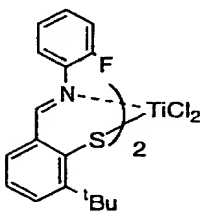
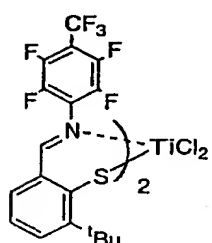
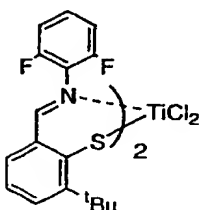
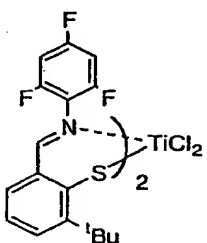
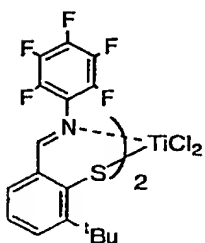
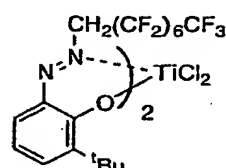
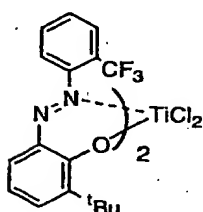
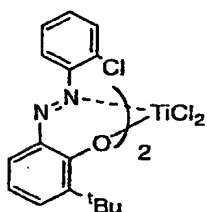
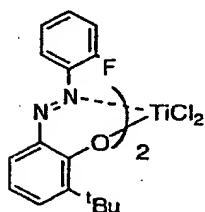
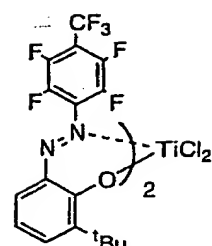
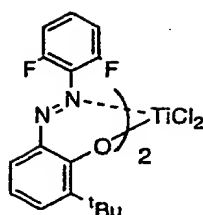
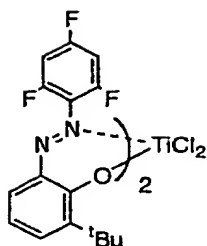
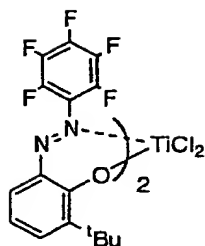


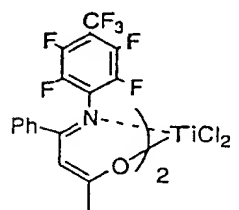
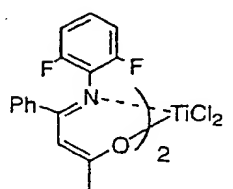
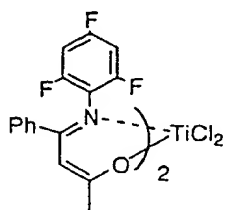
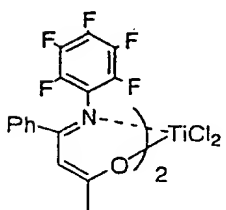
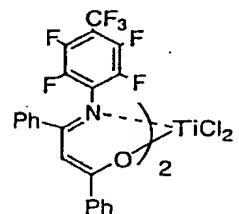
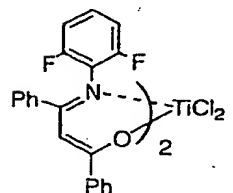
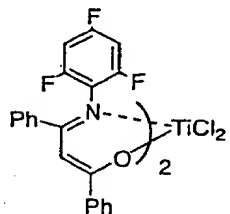
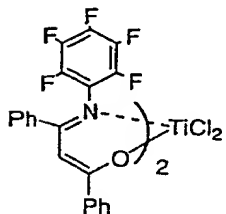
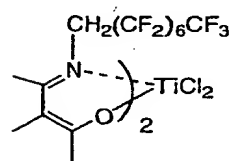
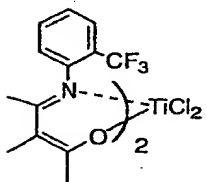
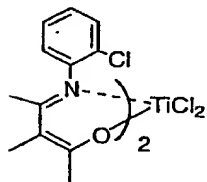
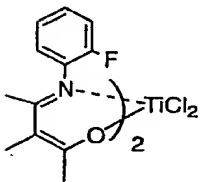
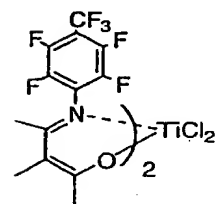
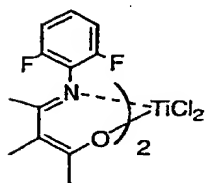
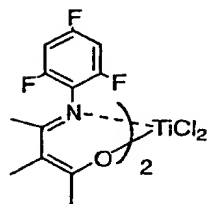
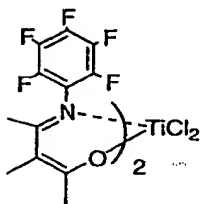
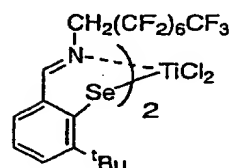
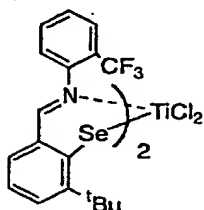
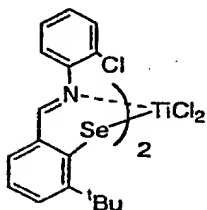
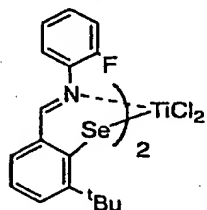
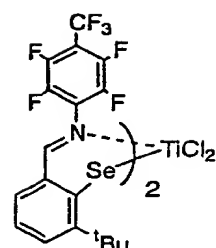
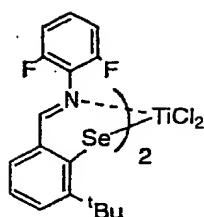
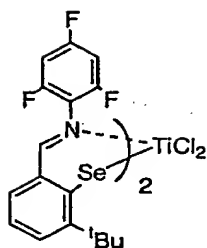
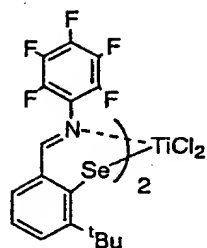
same atoms and groups as previously described with respect to X in the formula (I).

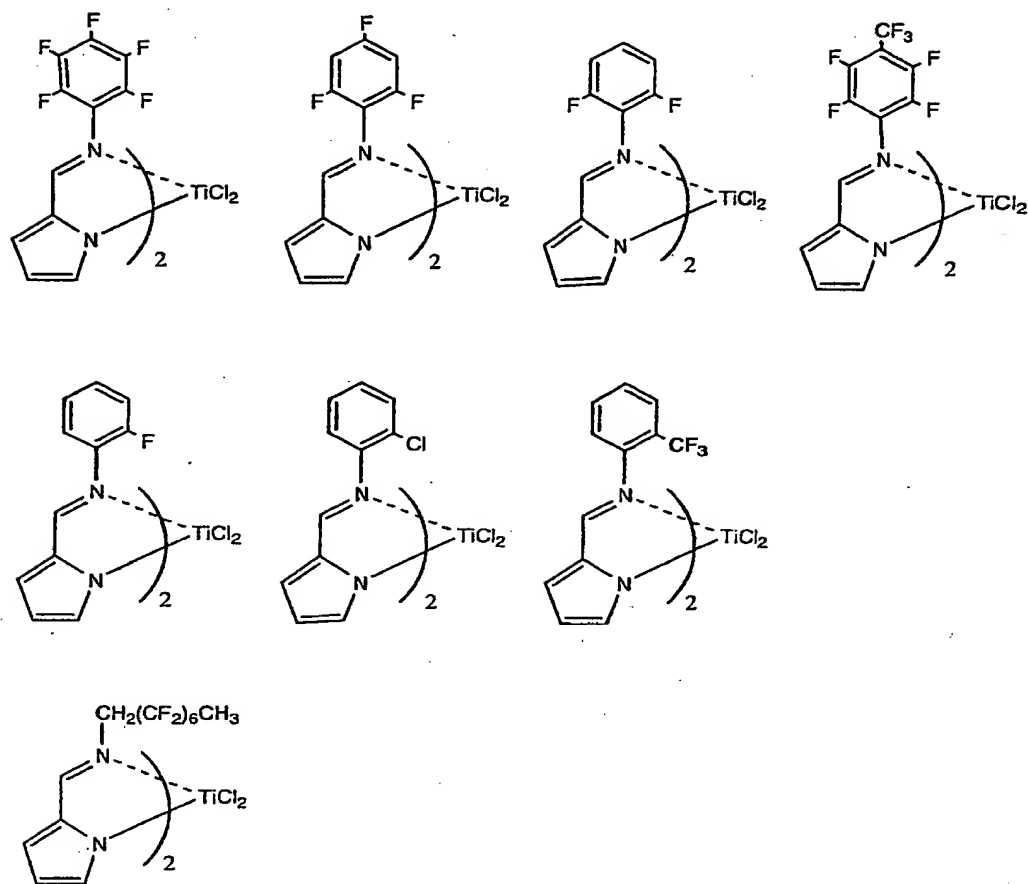
When n is 2 or greater, plural groups indicated by X may be the same or different, and plural groups indicated  
5 by X may be bonded to form a ring.

The transition metal compound represented by the formula (II-a'), (II-b') or (III') preferably has properties that, in a  $\beta$ -agostic structure of a cationic complex wherein one of X in the formula is replaced with  
10 a n-propyl group, said structure being measured by a density functional method, the distance between the heteroatom, which has no direct bond to the central metal M and is nearest to the central metal M, and hydrogen at the  $\beta$ -position is not more than 3.0 Å and the  
15 electrostatic energy is not more than 10 kJ/mol.

Examples of the transition metal compounds represented by the formula (I), (II-a), (II-b), (II-a'), (II-b'), (III) or (III) are given below, without limiting thereto.

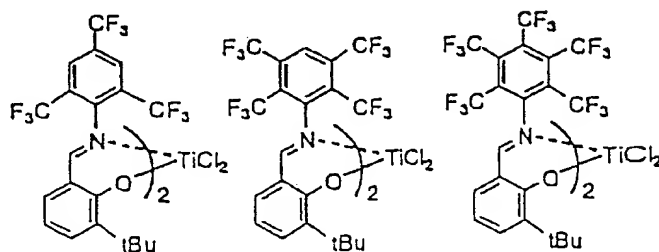
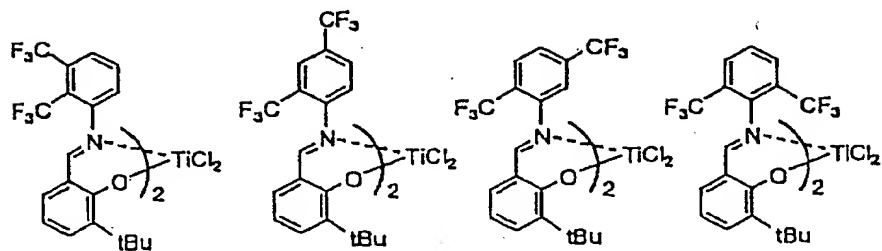
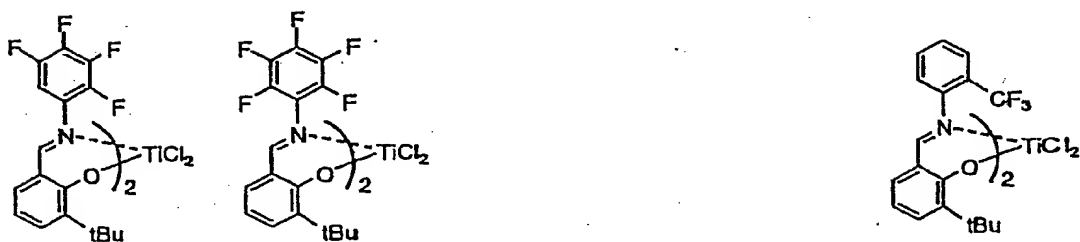
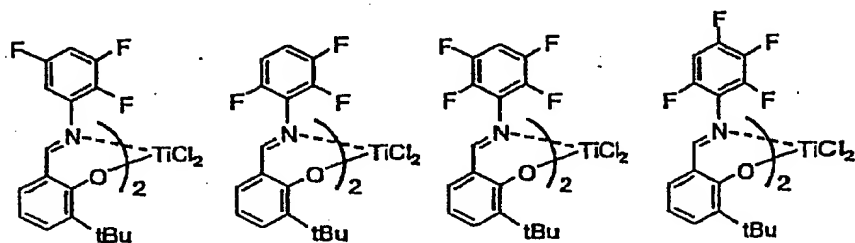
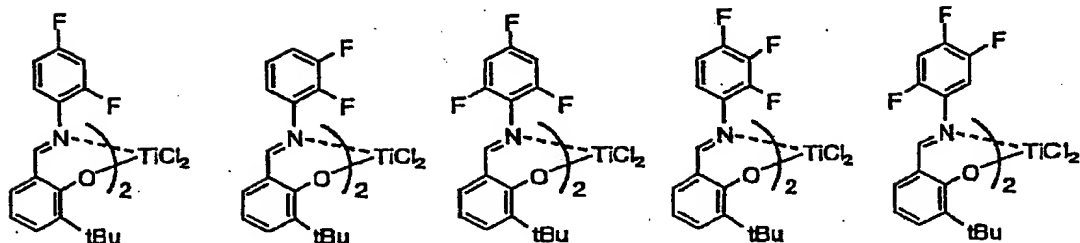
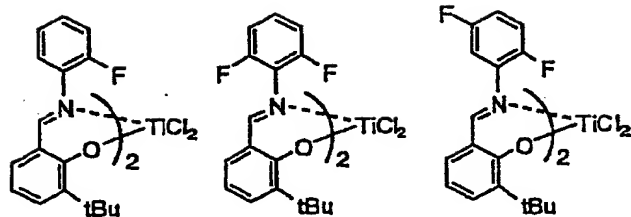




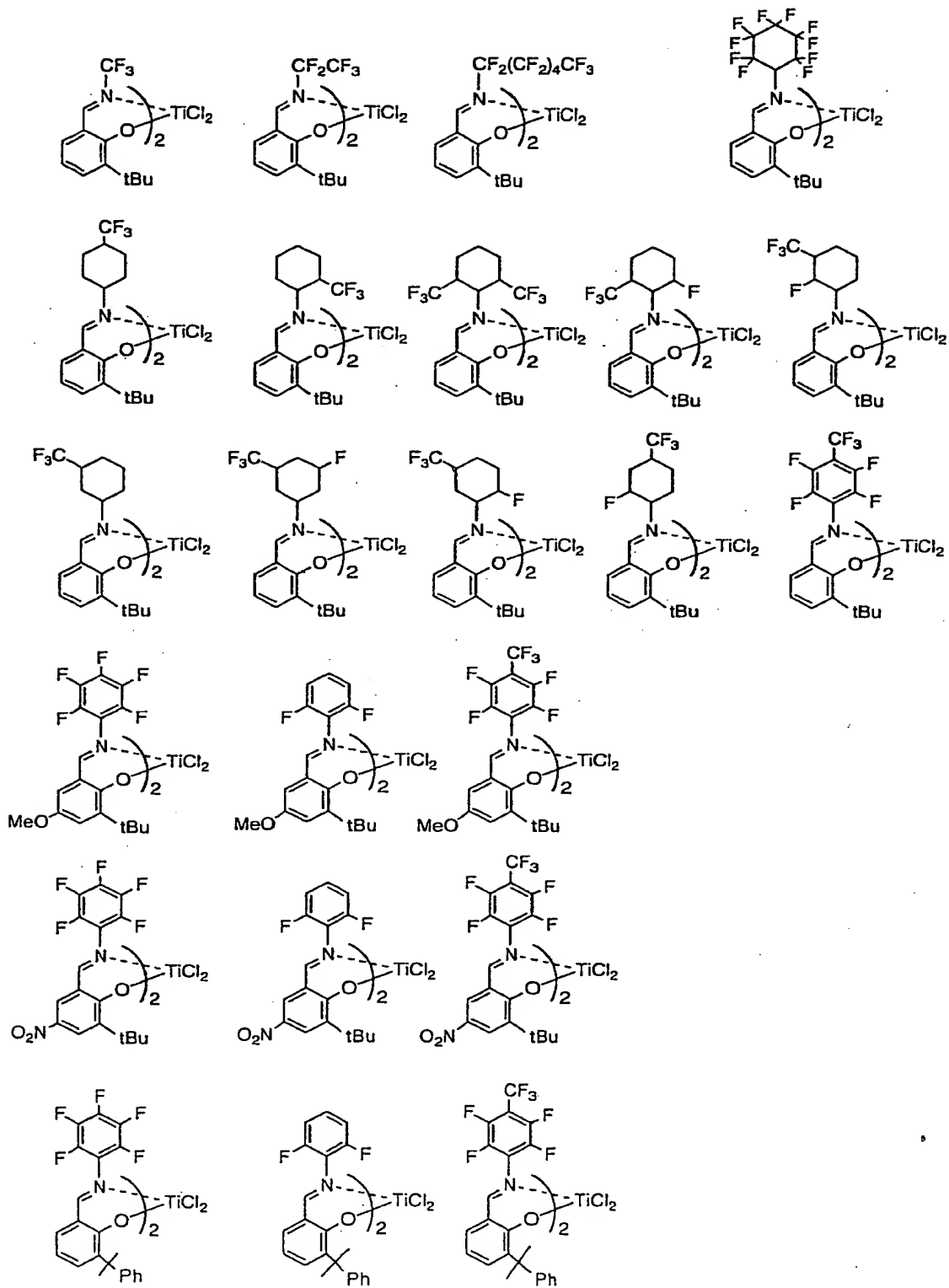


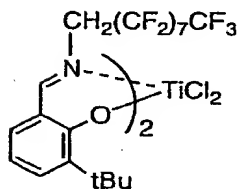
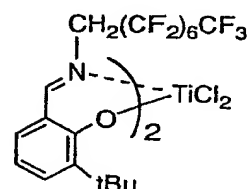
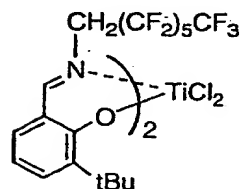
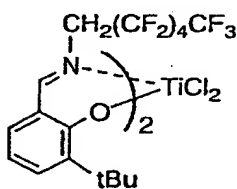
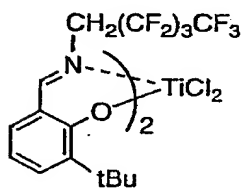
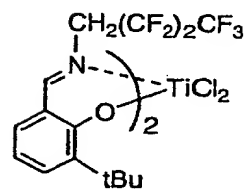
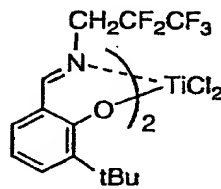
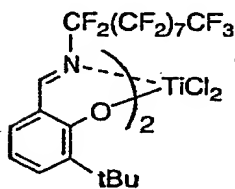
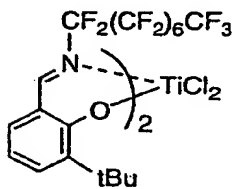
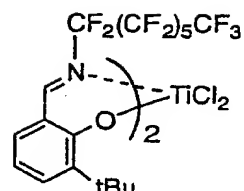
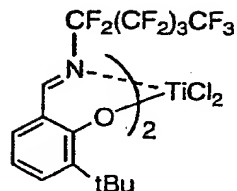
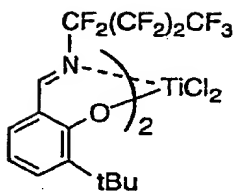
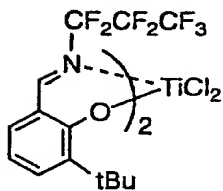
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In the above examples, Bu denotes a butyl group.

In the present invention, transition metal compounds wherein the titanium metal is replaced with a metal other than titanium, such as zirconium or hafnium, in the  
5 above-mentioned compounds are also employable.

The process for preparing the transition metal compound (A) is not specifically limited, and for example, the transition metal compound represented by the formula  
10 (III) can be synthesized by allowing a compound (ligand precursor) which becomes a ligand in the resulting transition metal compound to react with a transition metal  $M^1$ -containing compound represented by  $M^1X_k$  ( $M^1$  and X have the same meanings as those of  $M^1$  and X in the  
15 formula (III), and k is a number satisfying a valence of  $M^1$ ).

The ligand precursor is obtained by allowing a salicylaldehyde compound to react with a primary amine compound represented by the formula  $R^{10}-NH_2$  ( $R^{10}$  has the  
20 same meaning as previously described), such as an aniline compound or an alkylamine compound. More specifically, both of the starting compounds are dissolved in a solvent. As the solvent, a solvent usually used for such a reaction is employable, and above all, an alcohol solvent  
25 such as methanol or ethanol or a hydrocarbon solvent such

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as toluene is preferable. Then, the resulting solution is stirred for about 1 to 100 hours under the conditions of room temperature to a reflux temperature to obtain the corresponding ligand precursor. In the synthesis of the  
5 ligand precursor, an acid catalyst such as formic acid, acetic acid or toluenesulfonic acid may be used. Use of molecular sieves, magnesium sulfate or sodium sulfate as a dehydrating agent or dehydration by a Dean-Stark method is effective for the progress of the reaction.

10 Then, the ligand precursor thus obtained is allowed to react with a transition metal  $M^1$ -containing compound to synthesize the corresponding transition metal compound. More specifically, the ligand precursor thus synthesized is dissolved in a solvent, and if desired, the solution  
15 is contacted with a base to prepare a phenoxide salt. Then, the solution or the salt is mixed with a metallic compound such as a metallic halide or a metallic alkylate at a low temperature and stirred for about 1 to 48 hours at a temperature of  $-78^{\circ}\text{C}$  to room temperature or under  
20 the reflux conditions. As the solvent, a solvent usually used for such a reaction is employable, and above all, a polar solvent such as ether or tetrahydrofuran (THF) or a hydrocarbon solvent such as toluene is preferable. As the base used for preparing the phenoxide salt, a  
25 metallic salt such as a lithium salt (e.g., n-

butyllithium) or a sodium salt (e.g., sodium hydride) or an organic base such as triethylamine or pyridine is preferable.

Depending upon the properties of the compound, the  
5 ligand precursor can be allowed to directly react with the transition metal  $M^1$ -containing compound without preparation of the phenoxide salt, to synthesize the corresponding transition metal compound.

It is possible to replace the metal  $M^1$  in the  
10 synthesized transition metal compound with another transition metal in a conventional way. Further, when any one of  $R^{10}$  and  $R^{11}$  to  $R^{15}$  is H, a substituent other than H may be introduced in any stage of the synthesis.

It is possible to use the reaction solution of the  
15 ligand precursor and the transition metal  $M^1$ -containing compound as it is without isolating the transition metal compound.

A usual process for preparing the complex is described also in EP1008595A2.

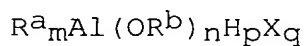
20 The transition metal compound (A) mentioned above can be used singly or in combination of two or more kinds.

#### (B-1) Organometallic compound

Examples of the organometallic compounds (B-1) which  
25 are optionally used in the invention include

organometallic compounds containing metals of Group 1, Group 2 and Group 13 of the periodic table, such as those described below.

- (B-1a) Organoaluminum compound represented by the  
 5 following formula:



- wherein  $R^a$  and  $R^b$  may be the same or different and are  
 10 each a hydrocarbon group of 1 to 15 carbon atoms, preferably 1 to 4 carbon atoms; X is a halogen atom; and m, n, p and q are numbers satisfying the conditions of  $0 < m \leq 3$ ,  $0 \leq n < 3$ ,  $0 \leq p < 3$ ,  $0 \leq q < 3$  and  $m+n+p+q = 3$ .

- (B-1b) Alkyl complex compound comprising a metal of  
 15 Group 1 and aluminum and represented by the following formula:



- 20 wherein  $M^2$  is Li, Na or K; and  $R^a$  is a hydrocarbon group of 1 to 15 carbon atoms, preferably 1 to 4 carbon atoms.

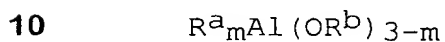
(B-1c) Compound represented by the following formula:

- 25  $R^a R^b M^3$

wherein  $R^a$  and  $R^b$  may be the same or different and are each a hydrocarbon group of 1 to 15 carbon atoms, preferably 1 to 4 carbon atoms; and  $M^3$  is Mg.

- 5        Examples of the organoaluminum compounds (B-1a) include:

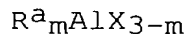
an organoaluminum compound represented by the following formula:



wherein  $R^a$  and  $R^b$  may be the same or different and are each a hydrocarbon group of 1 to 15 carbon atoms, preferably 1 to 4 carbon atoms, and  $m$  is preferably a

- 15        number satisfying the condition of  $1.5 \leq m \leq 3$ ;

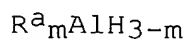
an organoaluminum compound represented by the following formula:



20

wherein  $R^a$  is a hydrocarbon group of 1 to 15 carbon atoms, preferably 1 to 4 carbon atoms,  $X$  is a halogen atom, and  $m$  is preferably a number satisfying the condition of  $0 < m < 3$ ;

an organoaluminum compound represented by the following formula:



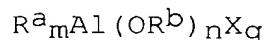
5

wherein  $R^a$  is a hydrocarbon group of 1 to 15 carbon atoms, preferably 1 to 4 carbon atoms, and  $m$  is preferably a number satisfying the condition of  $2 \leq m < 3$ ;

and

10

an organoaluminum compound represented by the following formula:



15 wherein  $R^a$  and  $R^b$  may be the same or different and are each a hydrocarbon group of 1 to 15 carbon atoms, preferably 1 to 4 carbon atoms,  $X$  is a halogen atom, and  $m$ ,  $n$  and  $q$  are numbers satisfying the conditions of  $0 < m \leq 3$ ,  $0 \leq n < 3$ ,  $0 \leq q < 3$  and  $m+n+q = 3$ .

20 Particular examples of the organoaluminum compounds (B-1a) include:

tri-n-alkylaluminums, such as trimethylaluminum, triethylaluminum, tri-n-butylaluminum, tripropylaluminum, tripentylaluminum, trihexylaluminum, trioctylaluminum and  
25 tridecylaluminum;

branched-chain trialkylaluminums, such as triisopropylaluminum, triisobutylaluminum, tri-sec-butylaluminum, tri-tert-butylaluminum, tri-2-methylbutylaluminum, tri-3-methylbutylaluminum, tri-2-methylpentylaluminum, tri-3-methylpentylaluminum, tri-4-methylpentylaluminum, tri-2-methylhexylaluminum, tri-3-methylhexylaluminum and tri-2-ethylhexylaluminum;

tricycloalkylaluminums, such as tricyclohexylaluminum and tricyclooctylaluminum;

10 triarylaluminums, such as triphenylaluminum and tritolylaluminum;

trialkenylaluminums, e.g., those represented by the formula  $(i-C_4H_9)_xAl_y(C_5H_{10})_z$  (wherein x, y and z are each a positive number, and  $z \geq 2x$ ), such as

15 triisoprenylaluminum;

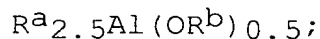
alkylaluminum alkoxides, such as isobutylaluminum methoxide, isobutylaluminum ethoxide and isobutylaluminum isopropoxide;

dialkylaluminum alkoxides, such as dimethylaluminum methoxide, diethylaluminum ethoxide and dibutylaluminum butoxide;

20

alkylaluminum sesquialkoxides, such as ethylaluminum sesquiethoxide and butylaluminum sesquibutoxide;

partially alkoxylated alkylaluminums, such as those having an average composition represented by



5 dialkylaluminum aryloxides, such as diethylaluminum phenoxide, diethylaluminum(2,6-di-t-butyl-4-methylphenoxide), ethylaluminumbis(2,6-di-t-butyl-4-methylphenoxide), diisobutylaluminum(2,6-di-t-butyl-4-methylphenoxide) and isobutylaluminumbis(2,6-di-t-butyl-4-methylphenoxide);

10 dialkylaluminum halides, such as dimethylaluminum chloride, diethylaluminum chloride, dibutylaluminum chloride, diethylaluminum bromide and diisobutylaluminum chloride;

15 alkylaluminum sesquihalides, such as ethylaluminum sesquichloride, butylaluminum sesquichloride and ethylaluminum sesquibromide,

partially halogenated alkylaluminums, e.g., alkylaluminum dihalide such as ethylaluminum dichloride, propylaluminum dichloride and butylaluminum dibromide;

20 dialkylaluminum hydrides, such as diethylaluminum hydride, dibutylaluminum hydride and diisobutylaluminum hydride;

partially hydrogenated alkylaluminums, e.g., alkylaluminum dihydrides, such as ethylaluminum dihydride  
25 and propylaluminum dihydride; and

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partially alkoxyated and halogenated alkylaluminums, such as ethylaluminum ethoxychloride, butylaluminum butoxychloride and ethylaluminum ethoxybromide.

Also employable are compounds analogous to the  
5 organoaluminum compound (B-1a). For example, there can be mentioned organoaluminum compounds wherein two or more aluminum compounds are combined through a nitrogen atom, such as  $(C_2H_5)_2AlN(C_2H_5)Al(C_2H_5)_2$ .

Examples of the compounds (B-1b) include  $LiAl(C_2H_5)_4$   
10 and  $LiAl(C_7H_{15})_4$ .

Other compounds, also employable as the organometallic compounds (B-1) include methyllithium, ethyllithium, propyllithium, butyllithium, methylmagnesium bromide, methylmagnesium chloride,  
15 ethylmagnesium bromide, ethylmagnesium chloride, propylmagnesium bromide, propylmagnesium chloride, butylmagnesium bromide, butylmagnesium chloride, dimethylmagnesium, diethylmagnesium, dibutylmagnesium and butylethylmagnesium. Combinations of compounds  
20 capable of producing the above-mentioned organoaluminum compounds in the polymerization system, e.g., a combination of halogenated aluminum and alkylolithium and a combination of halogenated aluminum and alkylmagnesium, are also employable.

Of the organometallic compounds (B-1), the organoaluminum compounds are preferable.

The organometallic compounds (B-1) mentioned above are used singly or in combination of two or more kinds.

5

(B-2) Organoaluminum oxy-compound

The organoaluminum oxy-compound (B-2) which is optionally used in the invention may be conventional aluminoxane or a benzene-insoluble organoaluminum oxy-  
10 compound such as exemplified in Japanese Patent Laid-Open Publication No. 78687/1990.

The conventional aluminoxane can be prepared by, for example, the following processes, and is generally obtained as a hydrocarbon solvent solution.

15 (1) An organoaluminum compound such as trialkylaluminum is added to a hydrocarbon medium suspension of a compound containing adsorption water or a salt containing water of crystallization, e.g., magnesium chloride hydrate, copper sulfate hydrate, aluminum  
20 sulfate hydrate, nickel sulfate hydrate or cerous chloride hydrate, to allow the organoaluminum compound to react with the adsorption water or the water of crystallization.

(2) Water, ice or water vapor is allowed to  
25 directly act on an organoaluminum compound such as

trialkylaluminum in a medium such as benzene, toluene, ethyl ether or tetrahydrofuran.

- (3) An organotin oxide such as dimethyltin oxide or dibutyltin oxide is allowed to react with an
- 5 organoaluminum compound such as trialkylaluminum in a medium such as decane, benzene or toluene.

- The aluminoxane may contain a small amount of an organometallic component. Further, it is possible that the solvent or the unreacted organoaluminum compound is
- 10 distilled off from the recovered solution of aluminoxane and the remainder is redissolved in a solvent or suspended in a poor solvent for aluminoxane.

- Examples of the organoaluminum compounds used for preparing the aluminoxane include the same organoaluminum
- 15 compounds as previously described with respect to the organoaluminum compound (B-1a). Of these, preferable are trialkylaluminums and tricycloalkylaluminums. Particularly preferable is trimethylaluminum.

- The organoaluminum compounds are used singly or in
- 20 combination of two or more kinds.

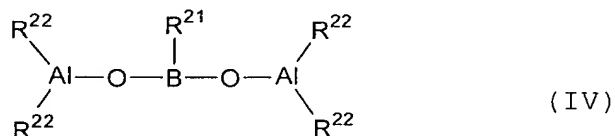
- Examples of the solvents used for preparing the aluminoxane include aromatic hydrocarbons, such as benzene, toluene, xylene, cumene and cymene; aliphatic hydrocarbons, such as pentane, hexane, heptane, octane,
- 25 decane, dodecane, hexadecane and octadecane; alicyclic

hydrocarbons, such as cyclopentane, cyclohexane, cyclooctane and methylcyclopentane; petroleum fractions, such as gasoline, kerosine and gas oil; and halogenated products of these aromatic, aliphatic and alicyclic

5 hydrocarbons (e.g., chlorinated or brominated products thereof). Also employable are ethers such as ethyl ether and tetrahydrofuran. Of the solvents, particularly preferable are aromatic hydrocarbons and aliphatic hydrocarbons.

10 The benzene-insoluble organoaluminum oxy-compound for use in the invention is preferably an organoaluminum oxy-compound containing an Al component which is soluble in benzene at 60 °C, in an amount of usually not more than 10 %, preferably not more than 5 %, particularly  
15 preferably not more than 2 %, in terms of Al atom. That is, the benzene-insoluble organoaluminum oxy-compound is preferably insoluble or sparingly soluble in benzene.

The organoaluminum oxy-compound for use in the invention is, for example, an organoaluminum oxy-compound  
20 containing boron and represented by the following formula (IV):



$$\mathbf{10} \quad \text{R}^{21}\text{-B-(OH)}_2 \quad (\text{V})$$

wherein R<sup>21</sup> is the same group as described above,  
to react with an organoaluminum compound in an inert  
solvent at a temperature of -80 °C to room temperature  
15 for 1 minute to 24 hours under an inert gas atmosphere.

Examples of the alkylboronic acids represented by the formula (V) include methylboronic acid, ethylboronic acid, isopropylboronic acid, n-propylboronic acid, n-butylboronic acid, isobutylboronic acid, n-hexylboronic acid, cyclohexylboronic acid, phenylboronic acid, 3,5-difluoroboronic acid, pentafluorophenylboronic acid and 3,5-bis(trifluoromethyl)phenylboronic acid. Of these, preferable are methylboronic acid, n-butylboronic acid, isobutylboronic acid, 3,5-difluorophenylboronic acid and pentafluorophenylboronic acid.

These alkylboronic acids are used singly or in combination of two or more kinds.

Examples of the organoaluminum compounds to be reacted with the alkylboronic acid include the same  
5 organoaluminum compounds as previously described with respect to the organoaluminum compound (B-1a). Of these, preferable are trialkylaluminums and tricycloalkylaluminums. Particularly preferable are trimethylaluminum, triethylaluminum and  
10 triisobutylaluminum. These organoaluminum compounds are used singly or in combination of two or more kinds.

The organoaluminum oxy-compounds (B-2) mentioned above are used singly or in combination of two or more kinds.

15

(B-3) Compound which reacts with the transition metal compound (A) to form ion pair

The compound (B-3) which reacts with a transition metal compound (A) to form an ion pair (referred to as  
20 "ionizing ionic compound" hereinafter), that is optionally used in the invention, includes Lewis acids, an ionic compounds, borane compounds and carborane compounds described in Japanese Patent Laid-Open Publications No. 501950/1989, No. 502036/1989, No.  
25 179005/1991, No. 179006/1991, No. 207703/1991 and No.

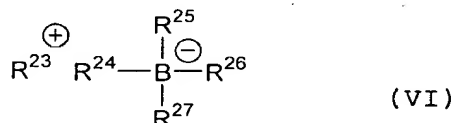
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207704/1991, and U.S. Patent No. 5,321,106. A heteropoly compound and an isopoly compound may also be employed.

The Lewis acids are, for example, compounds represented by  $BR_3$  (R is fluorine or a phenyl group which  
5 may have a substituent such as fluorine, methyl or trifluoromethyl). Examples of such compounds include trifluoroboron, triphenylboron, tris(4-fluorophenyl)boron, tris(3,5-difluorophenyl)boron, tris(4-fluoromethylphenyl)boron, tris(pentafluorophenyl)boron,  
10 tris(p-tolyl)boron, tris(o-tolyl)boron and tris(3,5-dimethylphenyl)boron.

The ionic compounds are, for example, compounds represented by the following formula (VI):

15



In the above formula,  $R^{23}$  is  $H^+$ , carbonium cation,  
20 oxonium cation, ammonium cation, phosphonium cation, cycloheptyltrienyl cation, ferrocenium cation having a transition metal, or the like.

$R^{24}$  to  $R^{27}$  may be the same or different and are each an organic group, preferably an aryl group or a  
25 substituted aryl group.

Examples of the carbonium cations include tri-substituted carbonium cations, such as triphenylcarbonium cation, tri(methylphenyl)carbonium cation and tri(dimethylphenyl)carbonium cation.

- 5 Examples of the ammonium cations include trialkylammonium cations, such as trimethylammonium cation, triethylammonium cation, tripropylammonium cation, tributylammonium cation and tri(n-butyl)ammonium cation; N,N-dialkylanilinium cations, such as N,N-
- 10 dimethylanilinium cation, N,N-diethylanilinium cation and N,N-2,4,6-pentamethylanilinium cation; and dialkylammonium cations, such as di(isopropyl)ammonium cation and dicyclohexylammonium cation.

- Examples of the phosphonium cations include
- 15 triarylphosphonium cations, such as triphenylphosphonium cation, tri(methylphenyl)phosphonium cation and tri(dimethylphenyl)phosphonium cation.

- R<sup>23</sup> is preferably carbonium cation or ammonium cation, particularly preferably triphenylcarbonium cation,
- 20 N,N-dimethylanilinium cation or N,N-diethylanilinium cation.

Also employable as the ionic compound is a trialkyl-substituted ammonium salt, a N,N-dialkylanilinium salt, a dialkylammonium salt or a triarylphosphonium salt.

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5 trimethylammoniumtetra(p-tolyl)boron,  
trimethylammoniumtetra(o-tolyl)boron, tri(n-  
butyl)ammoniumtetra(pentafluorophenyl)boron,  
tripropylammoniumtetra(o,p-dimethylphenyl)boron, tri(n-  
butyl)ammoniumtetra(m,m-dimethylphenyl)boron, tri(n-  
10 butyl)ammoniumtetra(p-trifluoromethylphenyl)boron, tri(n-  
butyl)ammoniumtetra(3,5-ditrifluoromethylphenyl)boron and  
tri(n-butyl)ammoniumtetra(o-tolyl)boron.

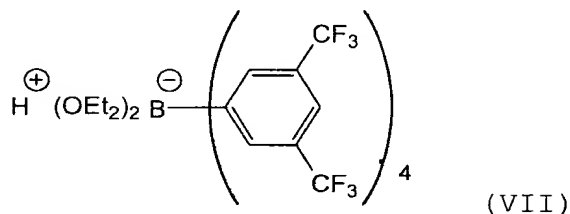
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Further employable as the ionic compounds are triphenylcarbeniumtetrakis(pentafluorophenyl)borate, N,N-dimethylaniliniumtetrakis(pentafluorophenyl)borate, ferroceniumtetra(pentafluorophenyl)borate, triphenylcarbeniumpentaphenylcyclopentadienyl complex,

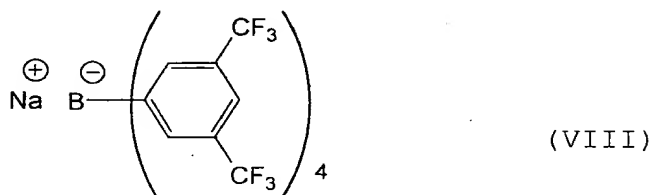
N,N-diethylaniliniumpentaphenylcyclopentadienyl complex  
and a boron compound represented by the formula (VII):

5



wherein Et is an ethyl group, or the formula (VIII):

10



Examples of the borane compounds include

15

salts of metallic carborane anions, such as

tri(n-butyl) ammoniumbis(nonahydrido-1,3-  
dicarbanonaborate) cobaltate(III),

tri(n-butyl) ammoniumbis(undecahydrido-7,8-  
dicarbaundecaborate) ferrate(III),

20

tri(n-butyl) ammoniumbis(undecahydrido-7,8-  
dicarbaundecaborate) cobaltate(III),

tri(n-butyl) ammoniumbis(undecahydrido-7,8-  
dicarbaundecaborate) nickelate(III),

tri(n-butyl) ammoniumbis(undecahydrido-7,8-

25

dicarbaundecaborate) cuprate(III),

- tri(n-butyl)ammoniumbis(undecahydrido-7,8-dicarbaundecaborate)aurate(III),
- tri(n-butyl)ammoniumbis(nonahydrido-7,8-dimethyl-7,8-dicarbaundecaborate)ferrate(III),
- 5 tri(n-butyl)ammoniumbis(nonahydrido-7,8-dimethyl-7,8-dicarbaundecaborate)chromate(III),
- tri(n-butyl)ammoniumbis(tribromooctahydrido-7,8-dicarbaundecaborate)cobaltate(III),
- tris[tri(n-butyl)ammonium]bis(undecahydrido-7-
- 10 carbaundecaborate)chromate(III),
- bis[tri(n-butyl)ammonium]bis(undecahydrido-7-carbaundecaborate)manganate(IV),
- bis[tri(n-butyl)ammonium]bis(undecahydrido-7-carbaundecaborate)cobaltate(III) and
- 15 bis[tri(n-butyl)ammonium]bis(undecahydrido-7-carbaundecaborate)nickelate(IV).

- The heteropoly compound comprises an atom of silicon, phosphorus, titanium, germanium, arsenic or tin and one or more atoms selected from vanadium, niobium, molybdenum
- 20 and tungsten. Examples of such compounds include phosphovanadic acid, germanovanadic acid, arsenovanadic acid, phosphoniobic acid, germanoniobic acid, silicomolybdic acid, phosphomolybdic acid, titanomolybdic acid, germanomolybdic acid, arsenomolybdic acid,
- 25 stannomolybdic acid, phosphotungstic acid,

- germanotungstic acid, stannotungstic acid,  
phosphomolybdovanadic acid, phosphotungstovanadic acid,  
germanotaungstovanadic acid, phosphomolybdotungstovanadic  
acid, germanomolybdotungstovanadic acid,  
5 phosphomolybdotungstic acid, phosphomolybdoniobic acid,  
metallic salts of these acids, specifically, salts of  
these acids, for example with metals of Group 1 or 2 of  
the periodic table such as lithium, sodium, potassium,  
rubidium, cesium, beryllium, magnesium, calcium,  
10 strontium and barium and organic salts of the above acids  
such as with triphenylethyl salt, but not limited thereto.

The ionizing ionic compounds (B-3) mentioned above  
may be used singly or in combination of two or more kinds.

- If the transition metal compound (A) is used as an  
15 olefin polymerization catalyst and an organoaluminum oxy-  
compound such as methylaluminumoxane is used as a co-  
catalyst component in combination with the compound (A),  
the olefin polymerization catalyst exhibits extremely  
high polymerization activity to olefins.

- 20 In the present invention, the transition metal  
compound represented by any one of the formulas (I), (II-  
a), (II-b) and (III) may be used singly as an olefin  
polymerization catalyst, or there may be used an olefin  
polymerization catalyst comprising:

- 25 (A) the transition metal compound, and

(B) at least one compound selected from:

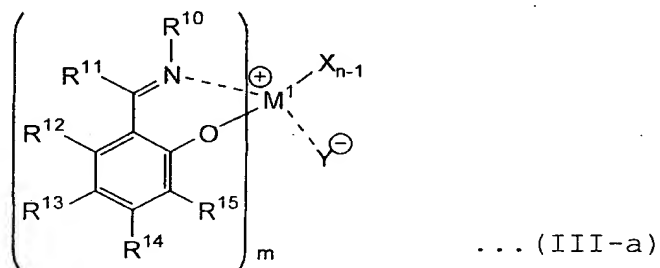
(B-1) an organoaluminum compound,

(B-2) an organoaluminum oxy-compound, and

(B-3) a compound which reacts with the

5 transition metal compound (A) to form an ion pair.

If the transition metal compound (A) represented by the formula (III) is used in combination with the component (B), a compound represented by the following formula (III-a) is formed in the polymerization system.



In the above formula,  $\text{R}^{10}$  to  $\text{R}^{15}$ ,  $\text{M}^1$ ,  $m$ ,  $n$  and  $X$  have the same meanings as those of  $\text{R}^{10}$  to  $\text{R}^{15}$ ,  $\text{M}^1$ ,  $m$ ,  $n$  and  $X$  in the formula (III), and  $Y$  is a so-called weak coordination anion.

20 In the formula (III-a), the bond between the metal  $\text{M}$  and  $Y$  may be a covalent bond or an ionic bond.

$Y$  is, for example, a weak coordination anion described in "Chemical Review", vol. 88, p. 1405 (1988), "Chemical Review", vol. 97, p. 927 (1993), or WO98/30612,

p. 6, and specific examples thereof include the following compounds:



- wherein each R may be the same or different and is an
- 5 oxygen atom, a nitrogen atom, a phosphorus atom, a hydrogen atom, a halogen atom, a substituent containing any of these atoms, an aliphatic hydrocarbon group, an aromatic hydrocarbon group, an alicyclic hydrocarbon group, a substituent wherein an aliphatic, aromatic or
- 10 alicyclic hydrocarbon group is substituted with an oxygen atom, a nitrogen atom, a phosphorus atom or a halogen atom, or a substituent wherein an aliphatic, aromatic or alicyclic hydrocarbon group is substituted with a substituent having an oxygen atom, a nitrogen atom, a
- 15 phosphorus atom or a halogen atom;



- wherein each R may be the same or different and is an oxygen atom, a nitrogen atom, a phosphorus atom, a halogen atom, a substituent containing any of these atoms,
- 20 an aliphatic hydrocarbon group, an aromatic hydrocarbon group, an alicyclic hydrocarbon group, a substituent wherein an aliphatic, aromatic or alicyclic hydrocarbon group is substituted with an oxygen atom, a nitrogen atom, a phosphorus atom or a halogen atom, or a substituent
- 25 wherein an aliphatic, aromatic or alicyclic hydrocarbon

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group is substituted with a substituent having an oxygen atom, a nitrogen atom, a phosphorus atom or a halogen atom;

- PF<sub>6</sub><sup>-</sup>; SbR<sub>5</sub><sup>-</sup>; trifluoromethane sulfonate; and p-toluene sulfonate.

The olefin polymerization catalyst employable in the invention can contain the following carrier (C) and/or the later-described organic compound (D), if necessary, in addition to the transition metal compound (A) and at least one compound (B) (sometimes referred to as a "component (B)" hereinafter) selected from the organometallic compound (B-1), the organoaluminum oxy-compound (B-2) and the ionizing ionic compound (B-3).

15

(C) Carrier

The carrier (C) optionally used in the invention is an inorganic or organic compound in the form of granular or particulate solid. As the inorganic compounds, porous oxides, inorganic halides, clay, clay minerals or ion-exchange layered compounds are preferable.

Examples of the porous oxides include SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, ZrO, TiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, CaO, ZnO, BaO, ThO<sub>2</sub>, and complex compounds or mixtures containing these oxides, such as natural or synthetic zeolite, SiO<sub>2</sub>-MgO, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>-TiO<sub>2</sub>, SiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub>, SiO<sub>2</sub>-Cr<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>-TiO<sub>2</sub>-MgO. Of these,

preferable are compounds containing  $\text{SiO}_2$  and/or  $\text{Al}_2\text{O}_3$  as the main component.

The inorganic oxides may contain small amounts of carbonate, sulfate, nitrate and oxide components, such as  
5  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{BaSO}_4$ ,  
 $\text{KNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Al}(\text{NO}_3)_3$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  and  $\text{Li}_2\text{O}$ .

Although the porous oxides differ in their properties depending upon the type and the preparation process thereof, the carrier preferably used in the  
10 invention has a particle diameter of 10 to 300  $\mu\text{m}$ , preferably 20 to 200  $\mu\text{m}$ , a specific surface area of 50 to 1,000  $\text{m}^2/\text{g}$ , preferably 100 to 700  $\text{m}^2/\text{g}$ , and a pore volume of 0.3 to 3.0  $\text{cm}^3/\text{g}$ . If necessary, the carrier may be calcined at 100 to 1,000  $^\circ\text{C}$ , preferably 150 to 700  $^\circ\text{C}$ ,  
15 prior to use.

Examples of the inorganic halides employable in the invention include  $\text{MgCl}_2$ ,  $\text{MgBr}_2$ ,  $\text{MnCl}_2$  and  $\text{MnBr}_2$ . The inorganic halide may be used as it is, or may be used after pulverized by, for example, a ball mill or an  
20 oscillating mill. The inorganic halide may also be used as fine particles of a obtained by dissolving the inorganic chloride in a solvent such as alcohol and then precipitating using a precipitant.

The clay employable as a carrier in the invention is  
25 generally composed mainly of clay minerals. The ion-



exchange layered-compounds employable as a carrier in the invention is compounds having a crystal structure wherein planes formed by ionic bonding or the like are laminated in parallel to one another with a weak bond strength, and

5 the ions contained therein are exchangeable. Most of clay minerals are ion-exchange layered compounds. The clay, the clay minerals and the ion-exchange layered compounds employable in the invention are not limited to natural ones but include synthetic ones.

10 Examples of such clay, clay minerals and ion-exchange layered compounds include clay, clay minerals and ion crystalline compounds having layered crystal structures such as hexagonal closest packing type, antimony type,  $\text{CdCl}_2$  type and  $\text{CdI}_2$  type.

15 Particular examples of the clay and the clay minerals include kaolin, bentonite, kibushi clay, gairome clay, allophane, hisingerite, pyrophyllite, mica, montmorillonite, vermiculite, chlorite, palygorskite, kaolinite, nacrite, dickite and halloysite. Particular

20 examples of the ion-exchange layered compounds include crystalline acid salts of polyvalent metals, such as  $\alpha\text{-Zr}(\text{HAsO}_4)_2 \cdot \text{H}_2\text{O}$ ,  $\alpha\text{-Zr}(\text{HPO}_4)_2$ ,  $\alpha\text{-Zr}(\text{KPO}_4)_2 \cdot 3\text{H}_2\text{O}$ ,  $\alpha\text{-Ti}(\text{HPO}_4)_2$ ,  $\alpha\text{-Ti}(\text{HAsO}_4)_2 \cdot \text{H}_2\text{O}$ ,  $\alpha\text{-Sn}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ ,  $\gamma\text{-Zr}(\text{HPO}_4)_2$ ,  $\gamma\text{-Ti}(\text{HPO}_4)_2$  and  $\gamma\text{-Ti}(\text{NH}_4\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ,

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The clay, the clay minerals and the ion-exchange layered compounds are preferably those having a pore volume, as measured on pores having a radius of not less than 20 Å by a mercury penetration method, of not less than 0.1 cc/g, and are particularly preferably those having a pore volume of 0.3 to 5 cc/g. The pore volume is measured on the pores having a radius of 20 to  $3 \times 10^4$  Å by a mercury penetration method using a mercury porosimeter.

10 If a compound having a pore volume, as measured on pores having a radius of not less than 20 Å, of less than 0.1 cc/g is used as the carrier, high polymerization activity tends to be hardly obtained.

It is also preferable that the clay and the clay minerals to be used in the invention are subjected to chemical treatments. Any of surface treatments, for example, to remove impurities attached to the surface and to influence on the crystal structure of the clay, are employable. Examples of such chemical treatments include acid treatment, alkali treatment, salt treatment and organic substance treatment. The acid treatment can contribute to not only removing impurities from the surface but also eluting cations such as Al, Fe and Mg present in the crystal structure to increase the surface area. The alkali treatment can destroy crystal structure

of clay to bring about change in the structure of the clay. The salt treatment and the organic substance treatment can produce, for example, ionic composites, molecular composites, or organic derivative to change the  
5 surface area or the distance between layers.

The ion-exchange layered compound for use in the invention may be a layered compound in which the exchangeable ions between layers have been exchanged with other large and bulky ions utilizing ion exchange  
10 properties to enlarge the distance between the layers. The bulky ion plays a pillar-like roll to support the layer structure and is generally called a "pillar". Introduction of other substances between layers of a layered compound is called "intercalation". Examples of  
15 the guest compounds to be intercalated include cationic inorganic compounds, such as  $\text{TiCl}_4$  and  $\text{ZrCl}_4$ ; metallic alkoxides, such as  $\text{Ti}(\text{OR})_4$ ,  $\text{Zr}(\text{OR})_4$ ,  $\text{PO}(\text{OR})_3$  and  $\text{B}(\text{OR})_3$  (R is a hydrocarbon group or the like); and metallic hydroxide ions, such as  $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}]^{7+}$ ,  $[\text{Zr}_4(\text{OH})_{14}]^{2+}$   
20 and  $[\text{Fe}_3\text{O}(\text{OCOCH}_3)_6]^+$ .

The compounds mentioned above may be used singly or in combination of two or more kinds.

The intercalation of the compounds may be carried out in the presence of polymers obtained by hydrolysis of  
25 metallic alkoxides such as  $\text{Si}(\text{OR})_4$ ,  $\text{Al}(\text{OR})_3$  and  $\text{Ge}(\text{OR})_4$

(R is a hydrocarbon group or the like) or in the presence of colloidal inorganic compounds such as  $\text{SiO}_2$ . Examples of the pillars include oxides produced by intercalation of the above-mentioned metallic hydroxide ions between  
5 layers, followed by dehydration under heating.

The clay, clay minerals and ion-exchange layered compounds mentioned above may be used as they are, or may be used after they are subjected to a treatment of ball milling, sieving or the like. Moreover, they may be used  
10 after they are subjected to water adsorption or dehydration under heating. The clay, clay minerals and ion-exchange layered compounds may be used singly or in combination of two or more kinds.

Of the above-mentioned materials, preferable are  
15 clay and clay minerals, and particularly preferable are montmorillonite, vermiculite, hectorite, tenorite and synthetic mica.

The organic compound is, for example, a granular or particulate solid compound having a particle diameter of  
20 10 to 300  $\mu\text{m}$ . Examples of such compounds include (co)polymers produced using an  $\alpha$ -olefin of 2 to 14 carbon atoms such as ethylene, propylene, 1-butene or 4-methyl-1-pentene as a main ingredient, (co)polymers produced using vinylcyclohexane or styrene as a main ingredient,  
25 and modified products thereof.

(D) Organic compound component

In the present invention, the organic compound component (D) is optionally used to improve

- 5 polymerizability and properties of the resulting polymer. Examples of the organic compounds include alcohols, phenolic compounds, carboxylic acids, phosphorus compounds and sulfonates, but not limited thereto.

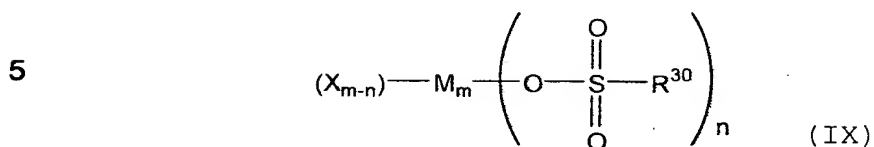
- 10 As the alcohols and the phenolic compounds, those represented by  $R^{28}-OH$  ( $R^{28}$  is a hydrocarbon group of 1 to 50 carbon atoms or a halogenated hydrocarbon group of 1 to 50 carbon atoms) are generally employed.

- 15 Preferable alcohols are those wherein  $R^{28}$  is a halogenated hydrocarbon group. Preferable phenolic compounds are preferably those wherein the  $\alpha, \alpha'$ -positions to the hydroxyl group are substituted with hydrocarbon groups of 1 to 20 carbon atoms.

- 20 As the carboxylic acids, those represented by  $R^{29}-COOH$  ( $R^{29}$  is a hydrocarbon group of 1 to 50 carbon atoms or a halogenated hydrocarbon group of 1 to 50 carbon atoms, preferably a halogenated hydrocarbon group of 1 to 50 carbon atoms) are generally employed.

- 25 As the phosphorus compounds, phosphoric acids having P-O-H bond, phosphates having P-OR bond or P=O bond and phosphine oxide compounds are preferably employed.

The sulfonates used in the invention are those represented by the following formula (IX):



In the above formula, M is an element of Group 1 to  
10 Group 14 of the periodic table.

$R^{30}$  is hydrogen, a hydrocarbon group of 1 to 20 carbon atoms or a halogenated hydrocarbon group of 1 to 20 carbon atoms.

X is a hydrogen atom, a halogen atom, a hydrocarbon  
15 group of 1 to 20 carbon atoms or a halogenated hydrocarbon group of 1 to 20 carbon atoms.

m is an integer of 1 to 7, and  $1 \leq n \leq 7$ .

In Fig. 1, an example of the process for preparing an olefin polymerization catalyst which is occasionally  
20 used in the present invention is shown.

Some examples of the processes are given below, though the methods to use the components and the order of feeding the components are optionally selected.

(1) The transition metal compound (A) is singly fed  
25 to the polymerization reactor.

(3) A catalyst component wherein the transition metal compound (A) is supported on the carrier (C) and the component (B) are fed to the polymerization reactor in an ordinary order.

(5) A catalyst component wherein the transition metal compound (A) and the component (B) are supported on the carrier (C) is fed to the polymerization reactor.

In the processes (4) and (5) in which the component (B) having been supported is used, the component (B) having been not supported may be added in an arbitrary order. In this case, these components (B) may be the same or different.

Onto the solid catalyst component wherein the transition metal compound (A) is supported on the carrier (C) or the transition metal compound (A) and the

component (B) are supported on the carrier (C), an olefin may be prepolymerized, and on the thus prepolymerized solid catalyst component, a catalyst component may be further supported.

- 5           In the olefin polymerization process according to the invention, an olefin of 2 to 20 carbon atoms is polymerized or copolymerized in the presence of the olefin polymerization catalyst to obtain a polymer. Examples of the olefins of 2 to 20 carbon atoms include
- 10           the same olefins as previously described.

          In the present invention, the polymerization can be carried out as any of liquid phase polymerization such as solution polymerization or suspension polymerization and gas phase polymerization.

- 15           Examples of inert hydrocarbon media used for the liquid phase polymerization include aliphatic hydrocarbons, such as propane, butane, pentane, hexane, heptane, octane, decane, dodecane and kerosine; alicyclic hydrocarbons, such as cyclopentane, cyclohexane and
- 20           methylcyclopentane; aromatic hydrocarbons, such as benzene, toluene and xylene; halogenated hydrocarbons, such as ethylene chloride, chlorobenzene and dichloromethane; and mixtures of these hydrocarbons. The olefin itself can be used as a solvent.



In the polymerization of an olefin of 2 to 20 carbon atoms using the olefin polymerization catalyst, the transition metal compound (A) is used in an amount of usually  $10^{-12}$  to 1 mol, preferably  $10^{-10}$  to  $10^{-2}$  mol, based on 1 liter of the reaction volume.

In the use of the component (B-1), the component (B-1) is used in such an amount that the molar ratio ((B-1)/M) of the component (B-1) to the transition metal atom (M) in the transition metal compound (A) becomes usually 0.01 to 100,000, preferably 0.05 to 50,000. In the use of the component (B-2), the component (B-2) is used in such an amount that the molar ratio ((B-2)/M) of the component (B-2) to the transition metal atom (M) in the transition metal compound (A) becomes usually 10 to 500,000, preferably 20 to 100,000. In the use of the component (B-3), the component (B-3) is used in such an amount that the molar ratio ((B-3)/M) of the component (B-3) to the transition metal atom (M) in the transition metal compound (A) becomes usually 1 to 10, preferably 1 to 5.

When the component (D) is used and the component (B-1) is used as the component (B), the component (D) is used in such an amount that the molar ratio ((D)/(B-1)) becomes usually 0.01 to 10, preferably 0.1 to 5. When the component (D) is used and the component (B-2) is used

as the component (B), the component (D) is used in such an amount that the molar ratio ((D)/(B-2)) becomes usually 0.001 to 2, preferably 0.005 to 1. When the component (D) is used and the component (B-3) is used as  
5 the component (B), the component (D) is used in such an amount that the molar ratio ((D)/(B-3)) becomes usually 0.01 to 10, preferably 0.1 to 5.

In the olefin polymerization using the olefin polymerization catalyst, the polymerization temperature  
10 is in the range of usually -40 to +200°C, preferably 0 to +100°C, and the polymerization pressure is in the range of usually atmospheric pressure to 100 kg/cm<sup>2</sup>, preferably atmospheric pressure to 50 kg/cm<sup>2</sup>. The polymerization reaction can be carried out by any one of batchwise,  
15 semi-continuous and continuous processes. It is possible to conduct the polymerization in two or more steps under the different reaction conditions.

The molecular weight of the resulting olefin polymer can be modified by controlling the monomer/catalyst ratio  
20 or the polymerization time.

By the process of the invention, an olefin polymer such as the aforesaid olefin polymer having a number-average molecular weight of not less than 500, preferably 500 to 10,000,000, more preferably 1,000 to 5,000,000,

and Mw/Mn of not more than 1.5, preferably not more than 1.3, is obtained.

According to the process of the invention, an olefin polymer having a high molecular weight and a narrow

5 molecular weight distribution can be obtained with high polymerization activity, or an olefin tapered polymer or an olefin block copolymer precisely controlled in the structure can be obtained with high polymerization activity.

10 Another embodiment of the process for preparing an olefin polymer according to the invention comprises contacting the polymer obtained as above with a functional group-containing compound to prepare such an olefin polymer having a functional group at the terminal  
15 as previously described. A compound capable of being converted into a functional group is included in the functional group-containing compound.

Examples of the functional group-containing compounds or the compounds capable of being converted  
20 into a functional group include compounds having functional groups such as an aromatic hydrocarbon group, a halogen atom, an oxygen-containing group, a nitrogen-containing group, a phosphorus-containing group and a metal atom-containing group. Specifically, there can be  
25 mentioned an aromatic vinyl compound, iodine, chlorine,

bromine, carbon dioxide, an ester compound, an aldehyde compound, a carboxylic acid compound, oxygen, an alkylamine compound, a silicon alkylhalide, an alkylaluminum compound, an alkylboron compound, an

5 alkylzinc compound, an alkyl lithium compound and the like.

After the contact with the functional group-containing compound, the functional group can be converted into another functional group by a known method.

In the contact of the olefin polymer with the

10 functional group-containing compound, the temperature is in the range of  $-78$  to  $+300^{\circ}\text{C}$ , preferably  $-78$  to  $+200^{\circ}\text{C}$ , and the pressure is in the range of usually atmospheric pressure to  $100\text{ kg/cm}^2$ , preferably atmospheric pressure to  $50\text{ kg/cm}^2$ . The contact time is in the range of

15 usually 1 minute to 100 hours, preferably 10 minutes to 24 hours.

The contact of the olefin polymer with the functional group-containing compound can be carried out in a solvent or without a solvent. Examples of the

20 solvents employable herein include aliphatic hydrocarbons, such as propane, butane, pentane, hexane, heptane, octane, decane, dodecane and kerosine; alicyclic hydrocarbons, such as cyclopentane, cyclohexene and methylcyclopentane; aromatic hydrocarbons, such as benzene, toluene and

25 xylene; halogenated hydrocarbons, such as ethylene

chloride, chlorobenzene and dichloromethane; oxygen-containing compounds, such as diethyl ether and tetrahydrofuran; and mixtures thereof.

A further embodiment of the process for preparing an  
5 olefin polymer according to the invention comprises  
polymerizing at least two olefins which are selected from  
olefins of 2 to 20 carbon atoms and have different  
polymerization reactivities, in the presence of an olefin  
polymerization catalyst comprising the aforesaid  
10 transition metal compound (A) to prepare a tapered  
polymer containing a segment wherein composition of two  
or more monomers continuously changes.

As described hereinbefore, the tapered polymer is a  
polymer in which the comonomer composition gradually  
15 changes from one end to the other end of the polymer  
chain. This polymer can be synthesized by polymerizing  
two or more monomers having different reactivities (e.g.,  
ethylene and propylene) in a living polymerization system  
wherein chain transfer reaction does not substantially  
20 take place.

Examples of the methods to feed the monomers include  
a method in which plural monomers are fed with  
continuously changing the monomer composition and a  
method in which plural monomers are fed together in the  
25 initial stage of the polymerization and a difference of

polymerization reactivities of the monomers is taken advantage of to obtain a tapered polymer. The temperature, pressure, addition of the catalyst and supporting on the carrier in the polymerization are the same as those described previously.

The two or more kinds of monomers are selected from the aforesaid olefins of 2 to 20 carbon atoms, they are preferably selected from ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene and 1-octene, and they are more preferably selected from ethylene, propylene and 1-butene.

A still further embodiment of the process for preparing an olefin polymer according to the invention comprises conducting the following step (1), the following step (2), and optionally, the following step (3) of an arbitrary number of times, to prepare an olefin block copolymer comprising plural polymer blocks.

In the step (1), at least one olefin selected from olefins of 2 to 20 carbon atoms is polymerized in the presence of the aforesaid olefin polymerization catalyst to prepare a polymer block.

Examples of the olefins of 2 to 20 carbon atoms include the same olefins as previously described, and they can be used singly or in combination of two or more

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kinds. Examples of the polymer blocks include the same blocks as previously described.

In the step (1), the polymerization temperature is in the range of usually  $-40$  to  $+200^{\circ}\text{C}$ , preferably  $0$  to  $+150^{\circ}\text{C}$ , and the polymerization pressure is in the range of usually atmospheric pressure to  $100\text{ kg/cm}^2$ , preferably atmospheric pressure to  $50\text{ kg/cm}^2$ .

In the step (2), at least one olefin selected from olefins of 2 to 20 carbon atoms is polymerized in the presence of the polymer block prepared in the step (1) to prepare a polymer block which is different from the polymer block prepared in the step (1).

The different polymer block means a polymer block which is different in at least one of primary structures, such as monomer type, comonomer type, comonomer composition, comonomer content, comonomer configuration and stereoregularity.

Examples of the olefins of 2 to 20 carbon atoms include the same olefins as previously described, and they can be used singly or in combination of two or more kinds. Examples of the polymer blocks obtained in the step (2) include the same blocks as previously described.

In the step (2), the polymerization temperature is in the range of usually  $-40$  to  $+200^{\circ}\text{C}$ , preferably  $0$  to  $+150^{\circ}\text{C}$ , and the polymerization pressure is in the range

of usually atmospheric pressure to 100 kg/cm<sup>2</sup>, preferably atmospheric pressure to 50 kg/cm<sup>2</sup>.

In the step (3), at least one olefin selected from olefins of 2 to 20 carbon atoms is polymerized in the presence of the polymer block prepared in the step (1) and the polymer block prepared in the step (2) to prepare a polymer block which is different from the polymer blocks prepared in the previous step.

Examples of the olefins of 2 to 20 carbon atoms include the same olefins as previously described, and they can be used singly or in combination or two or more kinds. Examples of the polymer blocks obtained in the step (3) include the same blocks as previously described.

In the step (3), the polymerization temperature is in the range of usually -40 to +200°C, preferably 0 to +150°C, and the polymerization pressure is in the range of usually atmospheric pressure to 100 kg/cm<sup>2</sup>, preferably atmospheric pressure to 50 kg/cm<sup>2</sup>.

The step (3) can be repeated arbitrary times with changing types of the olefins, combination thereof or polymerization conditions.

Through the process of the invention, for example, the aforesaid olefin block copolymer is obtained.

According to the process of the invention, an olefin block copolymer having a high molecular weight and a

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narrow molecular weight distribution can be obtained at a high polymerization temperature with high polymerization activity.

In the present invention, the block copolymer  
5 obtained above can be contacted with a functional group-containing compound to obtain an olefin block copolymer having a functional group at the terminal.

The contact of the olefin block copolymer with the functional group-containing compound is carried out in  
10 the same manner as previously described.

A still further embodiment of the process for preparing an olefin polymer according to the invention comprises polymerizing an olefin in the presence of a polymerization catalyst which promotes living  
15 polymerization of an olefin and further conducting olefin polymerization by the use of a catalyst obtained by cleaving a bond produced in the system between the catalyst and the resulting polymer chain by means of chain transfer reaction.

20 Promotion of the living polymerization can be confirmed by the narrow molecular weight distribution of the resulting polymer and the increase of the molecular weight of the resulting polymer with polymerization time. According to the process of the invention, it is feasible  
25 to prepare, for example, the monodisperse polyolefin, the

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olefin copolymer, the tapered polymer or the olefin copolymer mentioned above.

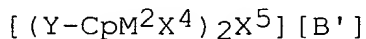
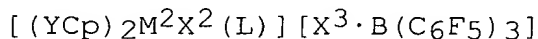
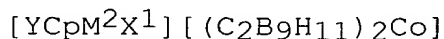
To confirm whether the living polymerization proceeds or not, it is most preferable to polymerize an  
5 olefin under the same conditions except for using no chain transfer agent.

To confirm whether the monodisperse polyolefin, the olefin copolymer, the tapered polymer or the olefin block copolymer can be prepared or not, it is most preferable  
10 to polymerize an olefin under the same conditions except for not performing a cleaving operation by the chain transfer reaction (i.e., the same conditions except for using no chain transfer agent).

In this process, the following olefin polymerization  
15 catalysts (1) to (5) are employable.

(1) An olefin polymerization catalyst comprising a Group 4 metallocene compound and a soluble non-coordination anionic compound

Examples of such catalysts include those of the  
20 following formulas..



In the above formulas,  $\text{M}^2$  is titanium, zirconium or  
25 hafnium,

Y is at least one hydrocarbon group of 1 to 20 carbon atoms,

Cp is a ligand having cyclopentadienyl skeleton, and when plural Cp are contained, they are the same or

5 different,

X<sup>1</sup> to X<sup>5</sup> are each the same as the aforesaid X,

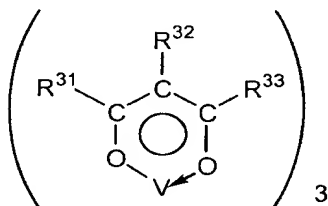
L is a Lewis acid, and

B' is the aforesaid non-coordination anion.

(2) An olefin polymerization catalyst that is a  
10 combination of (YCp)<sub>2</sub>SmX<sup>6</sup>, Y-CpTaX<sup>7</sup> or Y-CpNbX<sup>8</sup> (Y and Cp are each the same as that described above, and X<sup>6</sup> to X<sup>8</sup> are each the same as the aforesaid X) and methylaluminumoxane

(3) A compound represented by the following formula:

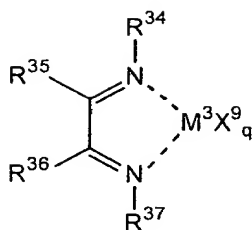
15



20 wherein R<sup>31</sup> to R<sup>33</sup> are each a hydrogen atom, an alkyl group of 1 to 8 carbon atoms or an aryl group, with the proviso that at least one of R<sup>31</sup> to R<sup>33</sup> needs to be a hydrogen atom but there is no case where R<sup>31</sup> to R<sup>33</sup> are all hydrogen atoms at the same time.

25

(4) Compound represented by the following formula:



5

In the above formula,  $\text{M}^3$  is a transition metal atom of Group 8 to Group 10 of the periodic table, preferably nickel, palladium or platinum.

$\text{R}^{34}$  to  $\text{R}^{37}$  may be the same or different and are each a hydrocarbon group of 1 to 50 carbon atoms, a halogenated hydrocarbon group of 1 to 50 carbon atoms, an organic silyl group, or a hydrocarbon group substituted with a substituent containing at least one element selected from nitrogen, oxygen, phosphorus, sulfur and silicon.

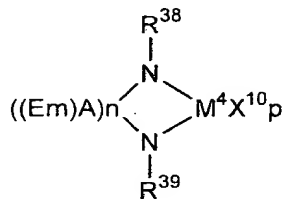
Two or more of the groups indicated by  $\text{R}^{34}$  to  $\text{R}^{37}$ , preferably adjacent groups, may be bonded to each other to form a ring.

$q$  is an integer of 0 to 4.

$\text{X}^q$  is a hydrogen atom, a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, an oxygen-containing group, a sulfur-containing group, a silicon-containing group or a nitrogen-containing group. When  $q$  is 2 or greater, plural groups  $\text{X}$  may be the same or different.

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(5) Compound represented by the following formula:



5

In the above formula,  $\text{M}^4$  is a transition metal atom of Group 3 to Group 6 of the periodic table, preferably titanium, zirconium or hafnium.

- 10  $\text{R}^{38}$  and  $\text{R}^{39}$  may be the same or different and are each a hydrogen atom, a hydrocarbon group of 1 to 50 carbon atoms, a halogenated hydrocarbon group of 1 to 50 carbon atoms, an organic silyl group, or a substituent having at least one element selected from nitrogen, oxygen,
- 15 phosphorus, sulfur and silicon.

$m$  is an integer of 0 or 2, and  $n$  is an integer of 1 to 5.

- A is an atom of Group 13 to Group 16 of the periodic table, specifically boron, carbon, nitrogen, oxygen,
- 20 silicon, phosphorus, sulfur, germanium, selenium, tin or the like, preferably carbon or silicon.

When  $n$  is 2 or greater, plural A may be the same or different.

- E is a substituent having at least one element
- 25 selected from carbon, hydrogen, oxygen, halogen, nitrogen,

sulfur, phosphorus, boron and silicon. When plural groups indicated by E exist, two of E may be the same or different, or may be bonded to each other to form a ring.

p is an integer of 0 to 4.

- 5         $X^{10}$  is a hydrogen atom, a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, an oxygen-containing group, a sulfur-containing group, a silicon-containing group or a nitrogen-containing group. When p is 2 or greater,
- 10 plural groups  $X^{10}$  may be the same or different.

- Examples of the olefin compounds of 1 to 20 carbon atoms for use in the polymerization include the same straight-chain or branched  $\alpha$ -olefins of 2 to 20 carbon atoms as previously described, cycloolefins of 3 to 20
- 15 carbon atoms, vinylcyclohexane, dienes, polyenes and aromatic vinyl compounds. These olefins can be used singly or in combination or two or more kinds.

- Also employable as the olefins in the present invention are monomers having atoms other than carbon and
- 20 hydrogen, and examples of such monomers include  $\alpha, \beta$ -unsaturated carboxylic acids, cycloolefin carboxylic acids, anhydrides thereof, metallic salts thereof, such as sodium salts, potassium salts, lithium salts, zinc salts, magnesium salts and calcium salts thereof,  $\alpha, \beta$ -
- 25 unsaturated carboxylic esters, vinyl esters, unsaturated

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glycidyls, halogenated olefins, unsaturated cyano compounds, unsaturated ketones, unsaturated ethers, functional group-containing styrene derivatives and vinyl group-containing heterocyclic compounds.

- 5 At least one olefin of the olefins employable in the invention is an olefin consisting of only carbon and hydrogen. There is no specific limitation on the quantity ratio of the olefin consisting of only carbon and hydrogen to the whole olefins, but for example, the
- 10 ratio is not less than 5 % by mol and not more than 100 % by mol based on the whole olefins. By the expression "at least one olefin" is meant that at least one kind of an olefin consisting of only carbon and hydrogen is contained in the whole olefin polymer of the invention,
- 15 and in case of, for example, an olefin polymer composed of plural polymer blocks, the olefin consisting of only carbon and hydrogen may be contained in any of the polymer blocks.

- In order to polymerize these olefins, the aforesaid
- 20 conditions are employable. The polymerization temperature is in the range of usually -100 to +200°C, preferably -78 to +150°C, and the polymerization pressure is in the range of usually atmospheric pressure to 100 kg/cm<sup>2</sup>, preferably atmospheric pressure to 50 kg/cm<sup>2</sup>.

The chain transfer reaction is promoted by maintaining the temperature at a given temperature at which the reaction proceeds or by using at least one compound selected from hydrogen, an organoaluminum compound, an organoboron compound, an organozinc compound, an organosilicon compound, an organocadmium compound and an organolead compound.

The conditions to promote the chain transfer reaction may be the same as or different from the above-mentioned olefin polymerization conditions. The temperature is in the range of usually  $-100$  to  $+200^{\circ}\text{C}$ , preferably  $-78$  to  $+150^{\circ}\text{C}$ , and the pressure is in the range of usually atmospheric pressure to  $100\text{ kg/cm}^2$ , preferably atmospheric pressure to  $50\text{ kg/cm}^2$ .

To promote the chain transfer reaction by heat, it is preferable that the olefin compound is polymerized at a temperature at which the chain transfer does not proceed, then the temperature of the reaction system is maintained at a given temperature at which the chain transfer proceeds to promote the chain transfer reaction, and the polymerization is conducted again at a temperature at which the chain transfer reaction does not proceed. This operation may be repeated arbitrary times.

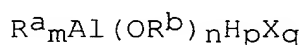
When the chain transfer reaction is promoted by the use of at least one compound selected from hydrogen, an



organoaluminum compound, an organoboron compound, an organozinc compound, an organosilicon compound, an organocadmium compound and an organolead compound, this reaction agent may be present from the beginning of the polymerization or may be added later in any stage. In the preparation of a tapered polymer or a block copolymer, it is preferable to add the chain transfer agent after the intended polymer is produced in the system.

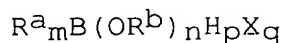
Examples of the chain transfer agents employable in the invention include hydrogen, an organoaluminum compound, an organoboron compound, an organozinc compound, an organosilicon compound, an organocadmium compound and an organolead compound. Specifically, there can be mentioned:

an organoaluminum compound represented by the formula:



wherein  $R^a$  and  $R^b$  may be the same or different, when plural  $R^a$  or plural  $R^b$  are present, they may be the same kind or two or more different kinds,  $R^a$  and  $R^b$  are each a hydrocarbon group of 1 to 15 carbon atoms, preferably 1 to 6 carbon atoms, X is a halogen atom, and m, n, p and q are numbers satisfying the conditions of  $0 < m \leq 3$ ,  $0 \leq n < 3$ ,  $0 \leq p < 3$ ,  $0 \leq q < 3$  and  $m+n+p+q=3$ ;

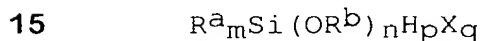
an organoboron compound represented by the following formula:



wherein  $R^a$  and  $R^b$  may be the same or different, when

- 5 plural  $R^a$  or plural  $R^b$  are present, they may be the same kind or two or more different kinds,  $R^a$  and  $R^b$  are each a hydrocarbon group of 1 to 15 carbon atoms, preferably 1 to 6 carbon atoms, X is a halogen atom, and m, n, p and q are numbers satisfying the conditions of  $0 < m \leq 3$
- 10 (preferably  $0 < m \leq 2$ ),  $0 \leq n < 3$  (preferably  $0 \leq n < 2$ ),  $0 \leq p < 3$  (preferably  $1 \leq p < 3$ ),  $0 \leq q < 3$  (preferably  $0 \leq p < 2$ ) and  $m+n+p+q=3$ ;

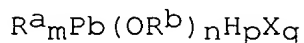
an organosilicon compound represented by the following formula:



wherein  $R^a$  and  $R^b$  may be the same or different, when

- plural  $R^a$  or plural  $R^b$  are present, they may be the same kind or two or more different kinds,  $R^a$  and  $R^b$  are each a hydrocarbon group of 1 to 15 carbon atoms, preferably 1
- 20 to 6 carbon atoms, X is a halogen atom, and m, n, p and q are numbers satisfying the conditions of  $0 < m \leq 4$  (preferably  $0 < m \leq 3$ ),  $0 \leq n < 4$  (preferably  $0 \leq n < 3$ ),  $0 \leq p < 4$  (preferably  $1 \leq p < 4$ ),  $0 \leq q < 4$  (preferably  $0 \leq p < 3$ ) and  $m+n+p+q=4$ ;

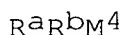
an organolead compound represented by the following formula:



wherein  $R^a$  and  $R^b$  may be the same or different, when

- 5 plural  $R^a$  or plural  $R^b$  are present, they may be the same kind or two or more different kinds,  $R^a$  and  $R^b$  are each a hydrocarbon group of 1 to 15 carbon atoms, preferably 1 to 6 carbon atoms, X is a halogen atom, and m, n, p and q are numbers satisfying the conditions of  $0 < m \leq 4$ ,  $0 \leq n < 4$ ,  $0 \leq p < 4$ ,  $0 \leq q < 4$  and  $m+n+p+q=4$ ; and
- 10

a dialkyl compound of zinc or cadmium, represented by the following formula:



- wherein  $R^a$  and  $R^b$  may be the same or different and are
- 15 each a hydrocarbon group of 1 to 15 carbon atoms, preferably 1 to 4 carbon atoms, and  $M^4$  is Zn or Cd.

- Specific examples of the above compounds include triakylaluminums, such as trimethylaluminum, triethylaluminum, tri-b-butylaluminum, trioctylaluminum,
- 20 tridecylaluminum, triisopropylaluminum and triisobutylaluminum, dialkylaluminum hydrides, such as diethylaluminum hydride, dibutylaluminum hydride and diisobutylaluminum hydride, alkylaluminum dihydrides, such as ethylaluminum dihydride and propylaluminum
- 25 dihydride, borane, borane tetrahydrofuran complex, borane

- dimethylsulfide complex, borane dimethylamine complex, borane trimethylamine complex, borane trimethylphosphine complex, thexyl borane, 9-borabicyclo[3.3.1]nonane, triethylborane, trimethylborane, monoalkylsilane,
- 5 dialkylsilane, trialkylsilane, diethylzinc, dimethylzinc, diethylcadmium, dimethylcadmium and tetraphenyllead.

Also employable are compounds by which the chain transfer agents are formed in the polymerization system.

- Of the above compounds, preferable are hydrogen, an
- 10 organozinc compound, an organoboron compound and an organosilicon compound, and particularly preferable are hydrogen, diethylzinc and a boron hydride compound.

The chain transfer agents mentioned above are used singly or in combination.

- 15 When the chain transfer agent is used, this agent is different from the organometallic compound used for forming an olefin polymerization catalyst, because the polymerization reaction in the present invention is characterized in that when the chain transfer agent is
- 20 not used, progress of living polymerization is essential, and the chain transfer reaction proceeds by the addition of the chain transfer agent.

The chain transfer agent is used in such an amount that the molar ratio of the chain transfer agent to the

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transition metal compound becomes usually 0.1 to 10000, preferably 1 to 5000.

The olefin polymerization catalyst used in the above process is preferably an olefin polymerization catalyst  
5 containing the transition metal compound (A), and the process for preparing the tapered polymer, the olefin copolymer or the olefin block copolymer is preferable.

According to the process of the invention, an olefin polymer having a high molecular weight and a narrow  
10 molecular weight distribution can be obtained with high polymerization activity, or a tapered polymer or an olefin block copolymer precisely controlled in the structure can be obtained with high polymerization activity.

15 To the monodisperse polyolefin, the olefin copolymer, the tapered polymer, the olefin block copolymer or a polymer having a functional group at the terminal of any of these polymers, various additives may be added.

The monodisperse polyolefin, the olefin copolymer,  
20 the tapered polymer, the olefin block copolymer or a polymer having a functional group at the terminal of any of these polymers can be applied to various uses.

A composition containing the monodisperse polyolefin, the olefin copolymer, the tapered polymer, the olefin  
25 block copolymer or a polymer having a functional group at

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the terminal of any of these polymers can be molded into articles by a known molding method.

Of the olefin polymers of the invention, the block copolymer containing a rigid block and a soft block and  
5 the tapered polymer have properties of thermoplastic elastomers.

Examples of the uses of the polymers include automobile parts, such as side malls, bumpers, weatherstrips, glass run channels, boots and air duct  
10 hoses; industrial parts, such as packings, mats, belts and hoses; electric/electronic parts, such as electric wires, codes and silencing gears; sporting goods, such as sport shoes, ski shoes; and civil engineering/building materials, such as gaskets and water barrier sheets.

15 To the olefin polymers of the invention, thermoplastic resins, fillers, nucleating agents and additives used for polymers may be added in arbitrary amounts, and the polymers may be subjected to secondary modification such as crosslinking or blowing.

20 As the thermoplastic resins, crystalline thermoplastic resins, such as polyolefin, polyamide, polyester and polyacetal; and non-crystalline thermoplastic resins, such as polystyrene, acrylonitrile/butadiene/styrene copolymer (ABS),  
25 polycarbonate, polyphenylene oxide and polyacrylate, are

employable. Polyvinyl chloride is also preferably employed.

Examples of the polyolefins include an ethylene polymer, a propylene polymer, a butene polymer, a 4-methyl-1-pentene polymer, a 3-methyl-1-butene polymer and a hexene polymer. Of these, an ethylene polymer, a propylene polymer and a 4-methyl-1-pentene polymer are preferable. As the ethylene polymer, an ethylene/polar-group containing vinyl copolymer is preferable.

10 Examples of the polyesters include aromatic polyesters, such as polyethylene terephthalate, polyethylene naphthalate and polybutylene terephthalate, polycaprolactone and polyhydroxybutyrate. Of these, polyethylene terephthalate is particularly preferable.

15 Examples of the polyamides include aliphatic polyamides, such as nylon-6, nylon-66, nylon-10, nylon-12 and nylon-46, and aromatic polyamides prepared from aromatic dicarboxylic acids and aliphatic diamines. Of these, nylon-6 is particularly preferable.

20 Examples of the polyacetals include polyformaldehyde (polyoxymethylene), polyacetaldehyde, polypropionaldehyde and polybutylaldehyde. Of these, polyformaldehyde is particularly preferable.

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The polystyrene may be a homopolymer of styrene or a bipolymer of styrene and acrylonitrile, methyl methacrylate or  $\alpha$ -methylstyrene.

As the ABS, preferably used is one comprising 20 to 5 35 % by mol of constituent units derived from acrylonitrile, 20 to 30 % by mol of constituent units derived from butadiene and 40 to 60 % by mol of constituent units derived from styrene.

Examples of the polycarbonates include polymers 10 obtained from bis(4-hydroxyphenyl)methane, 1,1-bis(4-hydroxyphenyl)ethane, 2,2-bis(4-hydroxyphenyl)propane and 2,2-bis(4-hydroxyphenyl)butane. Of these, polycarbonate obtained from 2,2-bis(4-hydroxyphenyl)propane is particularly preferable.

15 As the polyphenylene oxide, poly(2,6-dimethyl-1,4-phenyleneoxide) is preferably employed.

As the polyacrylate, polymethyl methacrylate or polybutyl acrylate is preferably employed.

The thermoplastic resins mentioned above may be used 20 singly or in combination or two or more kinds.

The olefin block copolymer of the invention may further contain, in addition to the thermoplastic resin, a crosslinking agent, a filler, a crosslinking accelerator, a crosslinking assistant, a softener, a 25 tackifier, an anti-aging agent, a blowing agent, a

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processing aid, an adhesion imparting agent, an inorganic filler, an organic filler, a nucleating agent, a heat stabilizer, a weathering stabilizer, an antistatic agent, a colorant, a lubricant, a flame retardant, an anti-  
5 blooming agent and the like.

#### Crosslinking agent

The crosslinking agent is, for example, sulfur, a sulfur compound or an organic peroxide. An organic peroxide having a temperature, at which the half-life  
10 period corresponds to 1 minute, of 130 to 200°C is preferable, and specifically, dicumyl peroxide, di-t-butyl peroxide, di-t-butyl peroxy-3,3,5-trimethylcyclohexane, t-butylcumyl peroxide, di-t-amyl peroxide, t-butyl hydroperoxide, 2,5-dimethyl-2,5-di-(t-butylperoxy)hexane or the like is preferable. When the  
15 organic peroxide is used as the crosslinking agent, it is preferable to use a crosslinking assistant in combination.

Of the various crosslinking agents, sulfur or a sulfur compound, particularly sulfur, is preferably used  
20 because a crosslinked product having excellent properties can be obtained. However, an organic peroxide is more preferably used because it has particularly excellent crosslinking efficiency.

#### Crosslinking accelerator

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As the crosslinking accelerator, N-cyclohexyl-2-benzothiazole sulfenamide (CBZ), N-oxydiethylene-2-benzothiazole sulfenamide, N,N-diisopropyl-2-benzothiazole sulfenamide, 2-mercaptobenzothiazole, 2-  
5 (2,4-dinitrophenyl)mercaptobenzothiazole or the like is employed.

#### Crosslinking assistant

The crosslinking assistant is used for organic peroxide crosslinking. Examples of the crosslinking  
10 assistants include sulfur; quinone dioxime compounds, such as p-quinone dioxime and p,p'-dibenzoylquinone dioxime; and polyfunctional monomers, such as (meth)acrylate compounds (e.g., trimethylolpropane triacrylate and polyethylene glycol dimethacrylate),  
15 allyl compounds (e.g., diallyl phthalate and triallyl cyanurate), maleimide compounds (e.g., N,N'-m-phenylenebismaleimide) and divinylbenzene.

#### Softener

As the softeners, those heretofore added to rubbers  
20 are widely used, and examples thereof include petroleum type softeners, such as process oil, lubricating oil, paraffin, liquid paraffin, petroleum asphalt and vaseline; coal tar type softeners, such as coal tar and coal tar pitch; aliphatic oil type softeners, such as  
25 castor oil, linseed oil, rapeseed oil and coconut oil;

tall oil; factice; waxes, such as beeswax, carnauba wax and lanoline; fatty acids and fatty acid salts, such as ricinolic acid, palmitic acid, barium stearate, calcium stearate and zinc laurate; and synthetic polymer

- 5 materials, such as petroleum resin, atactic polypropylene and coumarone-indene resin. Of these, petroleum type softeners are preferably employed, and process oil is particularly preferably employed.

Blowing agent

- 10 As the blowing agents, those generally used for blow-molding of rubbers are widely used, and examples thereof include inorganic blowing agents, such as sodium bicarbonate, sodium carbonate, ammonium bicarbonate, ammonium carbonate and ammonium nitrite; nitroso
- 15 compounds, such as N,N'-dimethyl-N'N'-dinitrosoterephthalamide and N,N'-dinitrosopentamethylenetetramine; azo compounds, such as azodicarbonamide, azobisisobutyronitrile, azocyclohexylnitrile, azodiaminobenzene and barium
- 20 azodicarboxylate; sulfonyl hydrazide compounds, such as benzenesulfonyl hydrazide, toluenesulfonyl hydrazide, p,p'-oxybis(benzenesulfonylhydrazide) and diphenylsulfon-3,3'-disulfonyl hydrazide; and azide compounds, such as calcium azide, 4,4-diphenyldisulfonyl azide and p-

5 with the blowing agent. Use of the blowing assistant in combination contributes to lowering of decomposition temperature of the blowing agent, acceleration of decomposition thereof and production of uniform bubbles. Examples of such blowing assistants include organic acids, such as salicylic acid, phthalic acid, stearic acid and oxalic acid; and urea or its derivatives.

## Processing aid

Adhesion imparting agent

Inorganic filler

- Examples of the inorganic fillers include silica, diatomaceous earth, alumina, titanium oxide, magnesium oxide, pumice powder, pumice balloon, aluminum hydroxide, magnesium hydroxide, basic magnesium carbonate, dolomite,
- 5 calcium sulfate, calcium titanate, barium sulfate, calcium sulfite, talc, clay, mica, asbestos, glass fiber, glass flake, glass bead, calcium silicate, montmorillonite, bentonite, graphite, aluminum powder and molybdenum sulfide.
- 10 Above all, layered compounds are preferably employed, and clay minerals having swelling/cleavage properties in dispersion media are particularly preferably employed. The clay minerals are generally classified into a type of two-layer structure consisting of a tetrahedral layer of
- 15 silica and an octahedral layer containing aluminum or magnesium as a central metal provided on the tetrahedral layer and a type of three-layer structure consisting of tetrahedral layers of silica and an octahedral layer containing aluminum or magnesium as a central metal
- 20 sandwiched between the tetrahedral layers. The two-layer structure type (former type) is, for example, a kaolinite group or an antigorite group, and the three-layer structure type (latter type) is, for example, a smectite group, a vermiculite group or a mica group that is
- 25 grouped according to the number of interlaminar cations.

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Specific examples of the clay minerals include kaolinite, dickite, nacrite, halloysite, antigorite, chrysotile, pyrophyllite, montmorillonite, beidellite, nontronite, saponite, sauconite, stevensite, hectorite, 5 tetrasilicic mica, sodium taeniorite, muscovite, margarite, talc, vermiculite, phlogopite, xanthophyllite and chlorite.

Clay minerals having been treated with organic materials (sometimes referred to as "organic modified 10 clay minerals") are also employable as the inorganic layered compounds. (On the clay minerals having been treated with organic materials, see "Dictionary of Clay" by Asakura Shoten.)

Of the above clay minerals, preferable are a 15 smectite group, a vermiculite group and a mica group, and more preferable is a smectite group, from the viewpoints of swelling properties or cleavage properties. Examples of the smectite group clay minerals include montmorillonite, beidellite, nontronite, saponite, 20 sauconite, stevensite and hectorite.

Examples of the dispersion media by which the inorganic layered compounds are swollen or cleaved are as follows. In case of the swelling clay minerals, there can be mentioned water, alcohols, such as methanol, 25 ethanol, propanol, isopropanol, ethylene glycol and

diethylene glycol, dimethylformamide, dimethyl sulfoxide and acetone. Of these, water and alcohol such as methanol are preferable.

In case of the organic modified clay minerals, there  
5 can be mentioned aromatic hydrocarbons, such as benzene, toluene and xylene, ethers, such as ethyl ether and tetrahydrofuran, ketones, such as acetone, methyl ethyl ketone and methyl isobutyl ketone, aliphatic hydrocarbons, such as n-pentane, n-hexane and n-octane, halogenated  
10 hydrocarbons, such as chlorobenzene, carbon tetrachloride, chloroform, dichloromethane, 1,2-dichloroethane and perchloroethylene, ethyl acetate, methyl methacrylate (MMA), dioctyl phthalate (DOP), dimethylformamide, dimethyl sulfoxide, methyl cellosolve and silicone oil.

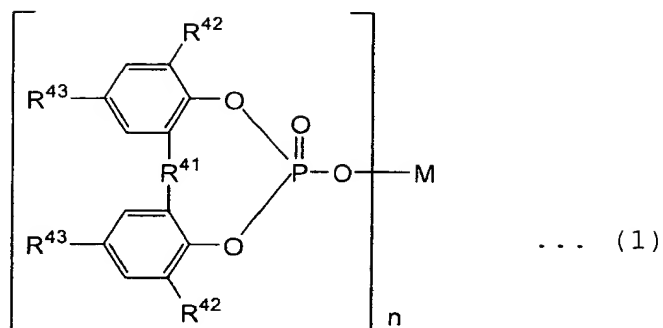
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#### Nucleating agent

As the nucleating agents, various nucleating agents hitherto known are used without specific limitation. Examples of the nucleating agents include the following aromatic phosphoric ester salt, benzylidenesorbitol,  
20 aromatic carboxylic acid and rosin nucleating agent.

Examples of aromatic phosphoric ester salt are compounds represented by the following formula (1).

5



In the above formula,  $\text{R}^{41}$  is an oxygen atom, a sulfur atom or a hydrocarbon group of 1 to 10 carbon atoms;  $\text{R}^{42}$  and  $\text{R}^{43}$  are each a hydrogen atom or hydrocarbon group of 1 to 10 carbon atoms and may be the same or different, and  $\text{R}^{42}\text{s}$ ,  $\text{R}^{43}\text{s}$  or  $\text{R}^{42}$  and  $\text{R}^{43}$  may be bonded to each other to form a ring; M is a metal atom having a valency of 1 to 3; and n is an integer of 1 to 3.

Concrete examples of the compounds represented by the above formula (1) include

sodium-2,2'-methylene-bis(4,6-di-t-butylphenyl)phosphate,

sodium-2,2'-ethylidene-bis(4,6-di-t-butylphenyl)phosphate,

lithium-2,2'-methylene-bis(4,6-di-t-butylphenyl)phosphate,

lithium-2,2'-ethylidene-bis(4,6-di-t-butylphenyl)phosphate,

sodium-2,2'-ethylidene-bis(4-i-propyl-6-t-butylphenyl)phosphate,

lithium-2,2'-methylene-bis(4-methyl-6-t-butylphenyl)phosphate,



lithium-2,2'-methylene-bis(4-ethyl-6-t-butylphenyl)phosphate,

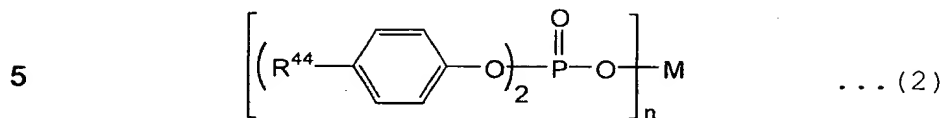
calcium-bis(2,2'-thiobis(4-methyl-6-t-butylphenyl)phosphate),

- 5 calcium-bis(2,2'-thiobis(4-ethyl-6-t-butylphenyl)phosphate),  
calcium-bis(2,2'-thiobis(4,6-di-t-butylphenyl)phosphate),  
magnesium-bis(2,2'-thiobis(4,6-di-t-butylphenyl)phosphate),  
10 magnesium-bis(2,2'-thiobis(4-t-octylphenyl)phosphate),  
sodium-2,2'-butylidene-bis(4,6-di-methylphenyl)phosphate,  
sodium-2,2'-butylidene-bis(4,6-di-t-butylphenyl)phosphate,  
sodium-2,2'-t-octylmethylene-bis(4,6-di-methylphenyl)phosphate,  
15 sodium-2,2'-t-octylmethylene-bis(4,6-di-t-butylphenyl)phosphate,  
calcium-bis(2,2'-methylene-bis(4,6-di-t-butylphenyl)phosphate),  
20 magnesium-bis(2,2'-methylene-bis(4,6-di-t-butylphenyl)phosphate),  
barium-bis(2,2'-methylene-bis(4,6-di-t-butylphenyl)phosphate),  
sodium-2,2'-methylene-bis(4-methyl-6-t-butylphenyl)phosphate,  
25 butylphenyl)phosphate,

- sodium-2,2'-methylene-bis(4-ethyl-6-t-butylphenyl)phosphate,  
sodium-(4,4'-dimethyl-5,6'-di-t-butyl-2,2'-biphenyl)phosphate,
- 5 calcium-bis-((4,4'-dimethyl-6,6'-di-t-butyl-2,2'-biphenyl)phosphate),  
sodium-2,2'-ethylidene-bis(4-m-butyl-6-t-butylphenyl)phosphate,  
sodium-2,2'-methylene-bis(4,6-di-methylphenyl)phosphate,
- 10 sodium-2,2'-methylene-bis(4,6-di-ethylphenyl)phosphate,  
potassium-2,2'-ethylidene-bis(4,6-di-t-butylphenyl)phosphate,  
calcium-bis(2,2'-ethylidene-bis(4,6-di-t-butylphenyl)phosphate),
- 15 magnesium-bis(2,2'-ethylidene-bis(4,6-di-t-butylphenyl)phosphate),  
barium-bis(2,2'-ethylidene-bis(4,6-di-t-butylphenyl)phosphate),  
aluminium-tris(2,2'-methylene-bis(4,6-di-t-butylphenyl)phosphate) and
- 20 aluminium-tris(2,2'-ethylidene-bis(4,6-di-t-butylphenyl)phosphate), and mixtures of two or more thereof. Particularly preferable is sodium-2,2'-methylene-bis(4,6-di-t-butylphenyl)phosphate.

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Examples of aromatic phosphoric ester salt are compounds represented by the following formula (2).



In the above formula,  $R^{44}$  is a hydrogen atom or hydrocarbon group of 1 to 10 carbon atoms; M is a metal atom having a valency of 1 to 3; and n is an integer of 1 to 3.

Concrete examples of the compounds represented by the above formula (2) include

sodium-bis(4-t-butylphenyl)phosphate,

sodium-bis(4-methylphenyl)phosphate,

15 sodium-bis(4-ethylphenyl)phosphate,

sodium-bis(4-i-propylphenyl)phosphate,

sodium-bis(4-t-octylphenyl)phosphate,

potassium-bis(4-t-butylphenyl)phosphate,

calcium-bis(4-t-butylphenyl)phosphate,

20 magnesium-bis(4-t-butylphenyl)phosphate,

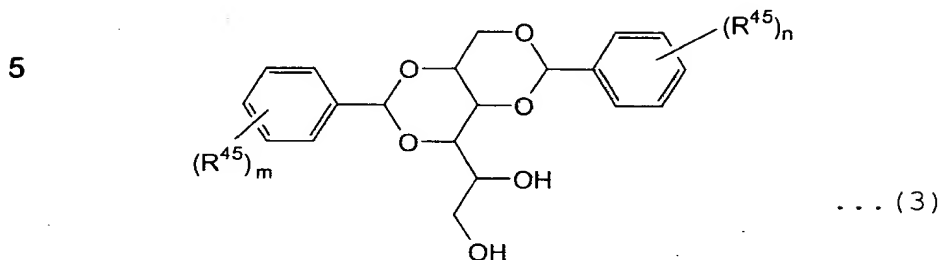
lithium-bis(4-t-butylphenyl)phosphate,

aluminum-bis(4-t-butylphenyl)phosphate, and

mixtures of two or more thereof. Particularly preferable is sodium-bis(4-t-butylphenyl)phosphate.

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The benzylidenesorbitol is, for example, a compound represented by the following formula (3):



wherein each  $R^{45}$  may be the same or different and is a  
 10 hydrogen atom or a hydrocarbon group of 1 to 10 carbon atoms, and  $m$  and  $n$  are each an integer of 0 to 5.

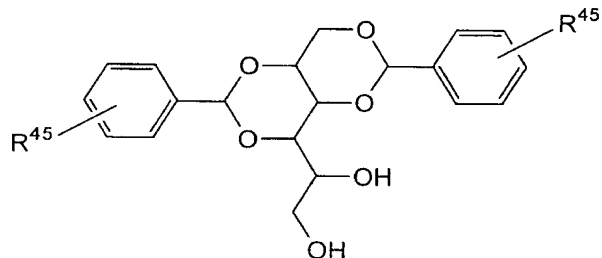
Examples of the compounds represented by the formula (3) include 1,3,2,4-dibenzylidenesorbitol, 1,3-benzylidene-2,4-p-methylbenzylidenesorbitol, 1,3-benzylidene-2,4-p-ethylbenzylidenesorbitol, 1,3-p-methylbenzylidene-2,4-benzylidenesorbitol, 1,3-p-ethylbenzylidene-2,4-benzylidenesorbitol, 1,3-p-methylbenzylidene-2,4-p-ethylbenzylidenesorbitol, 1,3-p-ethylbenzylidene-2,4-p-methylbenzylidenesorbitol,  
 15 1,3,2,4-di(p-methylbenzylidene)sorbitol, 1,3,2,4-di(p-ethylbenzylidene)sorbitol, 1,3,2,4-di(p-n-propylbenzylidene)sorbitol, 1,3,2,4-di(p-i-propylbenzylidene)sorbitol, 1,3,2,4-di(p-n-butylbenzylidene)sorbitol, 1,3,2,4-di(p-s-butylbenzylidene)sorbitol, 1,3,2,4-di(p-t-

20

25

- butylbenzylidene)sorbitol, 1,3,2,4-di(2',4'-  
dimethylbenzylidene)sorbitol, 1,3,2,4-di(p-  
methoxybenzylidene)sorbitol, 1,3,2,4-di(p-  
ethoxybenzylidene)sorbitol, 1,3-benzylidene-2-4-p-  
5 chlorobenzylidenesorbitol, 1,3-p-chlorobenzylidene-2-4-  
benzylidenesorbitol, 1,3-p-chlorobenzylidene-2-4-p-  
methylbenzylidenesorbitol, 1,3-p-chlorobenzylidene-2-4-p-  
ethylbenzylidenesorbitol, 1,3-p-methylbenzylidene-2-4-p-  
chlorobenzylidenesorbitol, 1,3-p-ethylbenzylidene-2-4-p-  
10 chlorobenzylidenesorbitol, 1,3,2,4-di(p-  
chlorobenzylidene)sorbitol, and mixtures of two or more  
of these compounds. Of these, preferable are 1,3,2,4-  
dibenzylidenesorbitol, 1,3,2,4-di(p-  
methylbenzylidene)sorbitol, 1,3,2,4-di(p-  
15 ethylbenzylidene)sorbitol, 1,3-p-chlorobenzylidene-2-4-p-  
methylbenzylidenesorbitol, 1,3,2,4-di(p-  
chlorobenzylidene)sorbitol, and mixtures of two or more  
of these compounds.

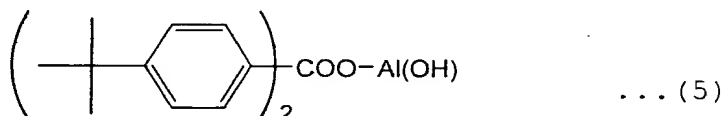
Of the above benzylidenesorbitols, preferable is a  
20 compound represented by the following formula (4):



... (4)

wherein each  $R^{45}$  may be the same or different and is methyl or ethyl.

- The aromatic carboxylic acid is, for example,  
 5 aluminumhydroxydipara-t-butyl benzoate represented by the following formula (5):



10

- The rosin type nucleating agent is, for example, a metallic salt of a rosin acid, and the metallic salt of a rosin acid is a reaction product of a rosin acid and a metallic compound. Examples of the rosin acids include  
 15 natural rosins, such as gum rosin, tall oil rosin and wood rosin; various modified rosins, such as disproportionated rosin, hydrogenated rosin, dehydrogenated rosin, polymerized rosin and  $\alpha, \beta$ -ethylenically unsaturated carboxylic acid-modified rosin;  
 20 purified products of the natural rosins; and purified products of the modified rosins. Examples of unsaturated carboxylic acids used for preparing the  $\alpha, \beta$ -ethylenically unsaturated carboxylic acid-modified rosins include  
 25 acid, itaconic anhydride, citraconic acid, acrylic acid

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- ad methacrylic acid. Of the above rosins, preferable is at least one rosin acid selected from the group consisting of a natural rosin, a modified rosin, a purified product of a natural rosin and a purified product of a modified rosin. The rosin acid contains plural resin acids selected from pimaric acid, sandarachpimaric acid, parastric acid, isopimaric acid, abietic acid, dehydroabietic acid, neoabietic acid, dihydropimaric acid, dihydroabietic acid and
- 5
- 10 tetrahydroabietic acid.

- The metallic compound which reacts with the rosin acid to form a metallic salt is, for example, a compound which contains a metallic element, such as sodium, potassium or magnesium, and forms a salt together with
- 15
- the rosin acid. Examples of the metallic salts include chlorides, nitrates, acetates, sulfates, carbonates, oxides and hydroxides of the above metals.

- Other examples of the nucleating agents include high-melting point polymers, metallic salts of aromatic
- 20
- carboxylic acids or aliphatic carboxylic acids, and inorganic compounds.

- Examples of the high-melting point polymers include polyvinylcycloalkanes, such as polyvinylcyclohexane and polyvinylcyclopentane, poly-3-methyl-1-pentene, poly-3-
- 25
- methyl-1-butene, and polyalkenylsilanes.

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- Examples of the metallic salts of aromatic carboxylic acids or aliphatic carboxylic acids include aluminum benzoate, aluminum p-t-butylbenzoate, sodium adipate, sodium thiophenecarboxylate and
- 5 pyrrolecarboxylic acid.

#### Molding method

- The olefin copolymer of the invention can be subjected to various molding methods such as extrusion molding, injection molding, blow molding, press molding
- 10 and stamping.

The olefin copolymer can be molded into sheets or films (unstretched) by extrusion molding.

- Stretched films can be obtained by stretching the extruded sheets or extruded films (unstretched) through
- 15 tentering (lengthwise-crosswise stretching, crosswise-lengthwise stretching), simultaneous biaxial orientation or monoaxial stretching. From the olefin copolymer of the invention, inflation films can also be produced.

- Filaments can be produced by, for example, extruding
- 20 a molten olefin copolymer through spinneret. The filaments may be produced by a melt blowing method.

- Injection molded products can be produced by injection molding the olefin copolymer into various shapes by the use of hitherto known injection molding
- 25 machines under the known conditions. The injection



molded products obtained from the olefin copolymer of the invention are hardly electrostatically charged and have excellent rigidity, heat resistance, impact resistance, surface gloss, chemical resistance and abrasion resistance, so that they can be broadly used as automobile interior trim, automobile exterior trim, housings of electric appliances, containers, etc.

Blow molded products can be produced by the use of hitherto known blow molding machines under the known conditions.

In the injection molding method, the olefin copolymer of the invention is injected into a parison mold at a resin temperature of 100 to 300°C to form a parison, then the parison is held in a mold of desired shape, and air is blown into the parison to fit the parison into the mold, whereby a blow molded product can be produced.

The stamping method is, for example, stamping molding. In this method, a base material and a skin material are press molded at the same time to perform integral molding (stamping molding), and the olefin copolymer can be used as the base material.

Use application

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The olefin copolymer of the invention can be applied to various uses, and for example, it can be used for film laminates, sheet laminates and modifiers.

Examples of the laminates containing at least one  
5 layer formed from the olefin copolymer of the invention include agricultural film, wrapping film, shrink film, protective film, separating film such as blood plasma separating film or water selective permeation vaporizing film, ion exchange film, battery separator, and selective  
10 separating film such as optical resolution film.

The olefin copolymer of the invention can be used as a modifier for rubbers.

Examples of the rubbers include crosslinked rubbers, such as natural rubber (NR), isoprene rubber (IR),  
15 butadiene rubber (BR), styrene/butadiene rubber (SBR), chloroprene rubber (CR), acrylonitrile/butadiene rubber (NBR), butyl rubber (IIR), ethylene/propylene rubber (EPM, EPDM), chlorosulfonated polyethylene (CSM), acrylic rubber (ACM, ANM, etc.), epichlorohydrin rubber (CO, ECO,  
20 etc.), silicone rubber (Q) and fluororubber (FKM, etc.); and thermoplastic rubbers, such as rubbers of styrene type, olefin type, urethane type, ester type, amide type and vinyl chloride type.

The olefin copolymer of the invention can be used as  
25 a modifier for lubricating oils, such as gasoline engine

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oil, diesel engine oil, marine engine oil, gear oil, machine oil, metal working oil, motor oil, machine oil, spindle oil and insulating oil. The olefin copolymer can be used as a viscosity modifier or a freezing point

5 depressant of these lubricating oils.

The olefin copolymer of the invention can be used as a modifier for waxes. Examples of the waxes include mineral waxes, such as montan wax, peat wax, ozokerite/ceresin wax and petroleum wax; synthetic waxes,  
10 such as polyethylene, Fischer-Tropsch wax, chemically modified hydrocarbon wax and substituted amide wax; vegetable waxes; and animal waxes.

The olefin copolymer of the invention can be used as a modifier for cement.

15 Examples of the cement include air setting cement, such as lime, gypsum and magnesia cement; water setting cement, such as Roman cement, natural cement, Portland cement, alumina cement and high sulfuric salt slag cement; and special cements, such as acid proof cement,  
20 refractory cement, water glass cement and dental cement.

Viscosity modifier, Moldability improver

The olefin polymer of the invention can be used as a viscosity modifier or a moldability improver for inks and paints, such as letterpress printing ink, lithographic  
25 printing ink, flexo graphic ink, gravure ink, oil paint,

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cellulose derivative paint, synthetic resin paint, water baking paint, powdery water paint and Japanese lacquer.

Building material, Civil engineering material

- The olefin copolymer of the invention can be used
- 5 for building/civil engineering resins and building/civil engineering molded products, such as flooring, floor tile, floor sheet, sound insulating sheet, heat insulating panel, damping material, decorative sheet, baseboard, asphalt modifier, gasket, sealing material, roofing sheet
- 10 and cut-off sheet.

Automobile interior or exterior trim, Gasoline tank

The olefin polymer of the invention can be used for automobile interior or exterior trim and gasoline tank.

Electric or electronic parts

- 15 The olefin copolymer of the invention can be used for electric or electronic parts. Examples of the electric or electronic parts include electric insulating materials, electronic part treating instruments, magnetic recording media, binders of magnetic recording media,
- 20 sealing materials of electric circuits, materials of electric appliances, base materials of containers such as electronic oven containers, films for electronic ovens, polymer electrolyte base materials and conductive alloy base materials. Other examples of the electric or
- 25 electronic parts include electric or electronic parts,

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- such as connector, socket, resistor, relay case switch coil bobbin, condenser, variable condenser case, optical pickup, optical connector, vibrator, various terminal assemblies, transformer, plug, printed wiring board,
- 5 tuner, speaker, microphone, headphone, small motor, magnetic head base, power module, housing, semiconductor, liquid crystal display parts, FDD carriage, FDD chassis, HDD parts, motor blush holder, parabola antenna and computer associated parts, VTR parts, TV parts, iron,
- 10 hair dryer, rice cooker parts, electronic oven parts, acoustic instrument parts, audio machine parts such as audio laser disc and compact disc, domestic or office electric appliance parts, such as light fitment parts, refrigerator parts, air conditioner parts, typewriter
- 15 parts and word processor parts, office computer associated parts, telephone associated parts, facsimile associated parts, copy machine associated parts, electromagnetic shielding material, speaker cone material, and vibrating element for speaker.

20 Aqueous emulsion

An aqueous emulsion containing the olefin copolymer of the invention can be used as an adhesive for polyolefins of excellent heat sealing properties.

Medical or hygienic material

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The olefin copolymer of the invention can be used for medical goods, such as nonwoven fabric, nonwoven fabric laminate, electret, medical tube, medical container, transfusion bag, prefill syringe and syringe, 5 medical materials, artificial organs, artificial muscles, filter films, food sanitation/health goods, retort bags, and freshness keeping films.

Miscellaneous goods

The olefin copolymer of the invention can be used 10 for stationery, such as desk mat, cutting mat, ruler, pen holder, pen grip, pen cap, scissors grip, cutter grip, magnet sheet, pen case, paper holder, binder, label seal, tape and white board; daily use miscellaneous goods, such as clothing, curtain, sheet, carpet, entrance hall mat, 15 bath mat, bucket, hose, bag, planter, air conditioner filter, exhaust fan filter, tableware, tray, cup, lunch box, coffee maker funnel, eyeglass frame, container, storage case, hanger, rope and washing net; sporting goods, such as shoes, goggles, skis, racket, ball, tent, 20 swimming goggles, swim fin, fishing rod, cooler box, leisure sheet and sporting net; toys, such as block and cards; containers, such as kerosine can, drum, detergent bottle and shampoo bottle; and display goods, such as signboard, pylon and plastic chain.

25 Filler modifier

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The olefin copolymer of the invention can be favorably used as an additive for preparing a filler dispersibility improver or a dispersibility-improved filler.

5 Compatibilizing agent

The olefin copolymer of the invention having a functional group at the terminal can be used as a compatibilizing agent. When the olefin copolymer of the invention is used as a compatibilizing agent, a  
10 polyolefin and a polar group-containing thermoplastic resin can be mixed in an arbitrary mixing ratio. The olefin copolymer has a polyolefin segment and a functional group, so that inherently incompatible components can be compatibilized with each other by the  
15 use of the copolymer.

Other uses

The olefin copolymer of the invention can be used for microcapsules, PTP packages, chemical bulbs, drug delivery system, etc.

20

EFFECT OF THE INVENTION

The olefin polymer according to the invention exhibits various useful properties.

According to the process for preparing an olefin  
25 polymer of the invention, an olefin polymer having a high

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molecular weight and a narrow molecular weight distribution and a tapered polymer or various block copolymers precisely controlled in the structure can be obtained at high polymerization temperatures with high polymerization activities.

#### EXAMPLE

The present invention is further described with reference to the following examples, but it should be construed that the invention is in no way limited to those examples.

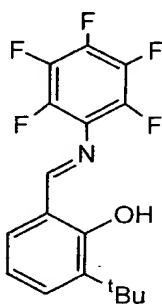
The structures of the compounds obtained in the synthesis examples were determined by means of  $^1\text{H}$ -NMR and FD-mass spectrometry (Japan Electron Optics Laboratory SX-102A).

#### Synthesis Example 1

In a 100 ml reactor thoroughly purged with nitrogen, 100 ml of toluene, 10.34 g (56.5 mmol) of pentafluoroaniline, 6.68 g (75.4 %, 28.2 mmol) of 3-t-butylsalicylaldehyde and a small amount of acetic acid as a catalyst were placed, and they were heated and refluxed with stirring for 7 hours. After the solution was allowed to stand for cooling, a small amount of p-toluenesulfonic acid was added as a catalyst, and they were refluxed with stirring for 2.5 hours. The reaction



solution was allowed to stand for cooling to room temperature, then filtered to remove the catalyst and vacuum concentrated. The residue was purified by a silica gel column to obtain 8.47 g (yield: 88 %) of yellow solids represented by the following formula (a).



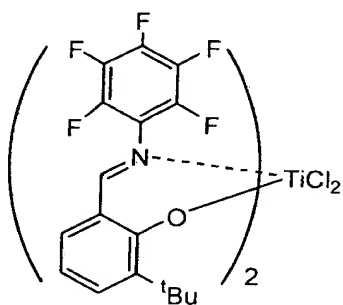
(a)

In a 50 ml reactor thoroughly purged with nitrogen, 1.043 g (3.00 mmol) of the compound (a) obtained above and 30 ml of anhydrous diethyl ether were placed, and the solution was cooled to  $-78^{\circ}\text{C}$  and stirred. To the solution, 2.05 ml of n-butyllithium (n-hexane solution, 1.54 N, 3.15 mmol) was dropwise added over a period of 5 minutes, and then the mixture was slowly heated to room temperature. After stirring for 3 hours at room temperature, the reaction solution was slowly added to an ether slurry of 3.00 ml of titanium tetrachloride (heptane solution, 0.5 M, 1.50 mmol) having been cooled to  $-78^{\circ}\text{C}$ . After the addition, the mixture was slowly heated to room temperature. The resulting dark red slurry was filtered, and the filtrate was vacuum

concentrated until the amount of the liquid became about 5 ml. The solids precipitated were collected and washed with hexane. The resulting solids were vacuum dried to obtain 0.381 g (yield: 32 %) of a brown compound

5 represented by the following formula (1). The FD-mass spectrometry of the compound (1) resulted in 802 (M+).

10



(1)

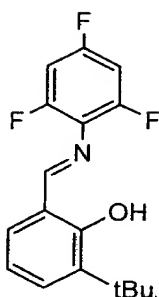
### Synthesis Example 2

15 In a 200 ml reactor thoroughly purged with nitrogen, 100 ml of toluene, 3.82 g (26.0 mmol) of 2,4,6-trifluoroaniline, 2.32 g (13.0 mmol) of 3-*t*-butylsalicylaldehyde and a small amount of *p*-toluenesulfonic acid as a catalyst were placed, and they

20 were heated and refluxed with stirring for 4 hours. The reaction solution was allowed to stand for cooling to room temperature, then filtered to remove the catalyst and vacuum concentrated. The residue was purified by a silica gel column to obtain 3.79 g (yield: 95 %) of a

25 yellow oil represented by the following formula (b).

5



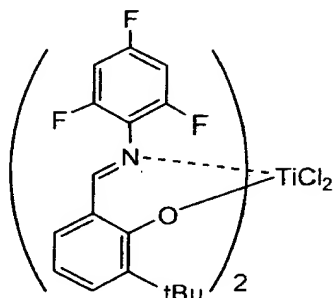
(b)

In a 50 ml reactor thoroughly purged with nitrogen, 1.23 g (4.00 mmol) of the compound (b) obtained above and 30 ml of anhydrous diethyl ether were placed, and the solution was cooled to  $-78^{\circ}\text{C}$  and stirred. To the solution, 2.63 ml of n-butyllithium (n-hexane solution, 1.60 N, 4.20 mmol) was dropwise added over a period of 5 minutes, and then the mixture was slowly heated to room temperature. After stirring for 2 hours at room temperature, the reaction solution was slowly added to an ether slurry of 4.00 ml of titanium tetrachloride (heptane solution, 0.5 M, 1.50 mmol) having been cooled to  $-78^{\circ}\text{C}$ . After the addition, the mixture was slowly heated to room temperature. The resulting dark red slurry was filtered, and the filtrate was vacuum concentrated. Then, 5 ml of ether and 30 ml of hexane were added, and the solids precipitated were collected and washed with hexane. The resulting solids were vacuum dried to obtain 0.550 g (yield: 38 %) of a reddish brown compound represented by the following formula (2). The

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FD-mass spectrometry of the compound (2) resulted in 730 (M+).

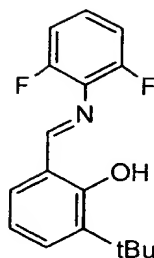
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(2)

### Synthesis Example 3

- 10 In a 100 ml reactor thoroughly purged with nitrogen, 30 ml of ethanol, 5.16 g (40.0 mmol) of 2,6-difluoroaniline, 3.58 g (20.0 mmol) of 3-t-butylsalicylaldehyde and a small amount of acetic acid as a catalyst were placed, and they were heated and refluxed
- 15 with stirring. With further adding a small amount of acetic acid, the mixture was refluxed with stirring for 150 hours. The reaction solution was allowed to stand for cooling to room temperature and then vacuum concentrated. The residue was purified by a silica gel
- 20 column to obtain 4.76 g (yield: 82.2 %) of yellow solids represented by the following formula (c).



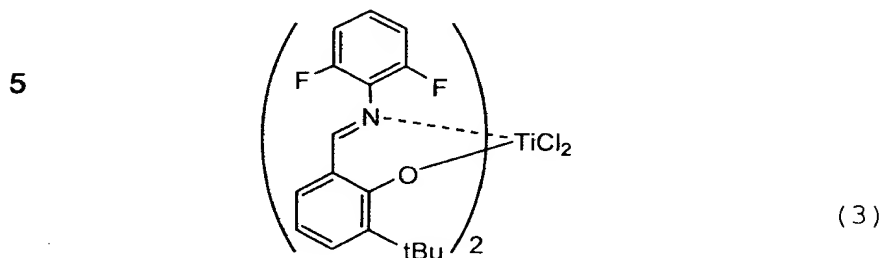
(c)

5

In a 30 ml reactor thoroughly purged with nitrogen, 1.16 g (4.00 mmol) of the compound (c) obtained above and 20 ml of anhydrous diethyl ether were placed, and the solution was cooled to  $-78^{\circ}\text{C}$  and stirred. To the solution, 2.50 ml of n-butyllithium (n-hexane solution, 1.6 N, 4.00 mmol) was dropwise added over a period of 5 minutes, and then the mixture was slowly heated to room temperature. After stirring for 3 hours at room temperature, the reaction solution was slowly added to an ether slurry of 4.00 ml of titanium tetrachloride (heptane solution, 0.5 M, 2.00 mmol) having been cooled to  $-78^{\circ}\text{C}$ . After the addition, the mixture was slowly heated to room temperature. The resulting dark red slurry was filtered, and the solids obtained were washed with a small amount of methylene chloride. The filtrate and the washing liquid were vacuum concentrated, and the resulting solids were collected and suspended in 15 ml of ether. The precipitate was filtered and then washed with a small amount of ether and hexane. The resulting solids were vacuum dried to obtain 1.059 g (yield: 76 %) of a

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brown compound represented by the following formula (3).  
The FD-mass spectrometry of the compound (3) resulted in  
694 (M+).

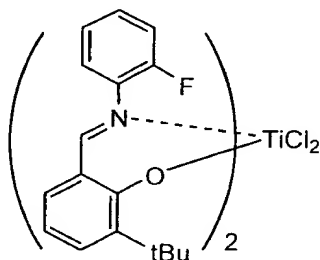


#### Synthesis Example 4

- 10 In a 200 ml reactor thoroughly purged with nitrogen,  
100 ml of toluene, 2.89 g (26.0 mmol) of o-fluoroaniline,  
2.32 g (13.0 mmol) of 3-t-butylsalicylaldehyde and a  
small amount of p-toluenesulfonic acid as a catalyst were  
placed, and they were heated and refluxed with stirring  
15 for 5 hours. The reaction solution was allowed to stand  
for cooling to room temperature, then filtered to remove  
the catalyst and vacuum concentrated. The residue was  
purified by a silica gel column to obtain 3.45 g (yield:  
98 %) of a yellow oil represented by the following  
20 formula (d).



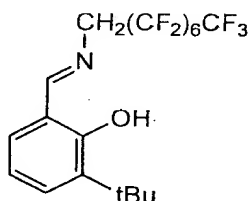
- In a 30 ml reactor thoroughly purged with nitrogen, 1.01 g (4.00 mmol) of the compound (d) obtained above and 30 ml of anhydrous diethyl ether were placed, and the solution was cooled to  $-78^{\circ}\text{C}$  and stirred. To the
- 5 solution, 2.63 ml of n-butyllithium (n-hexane solution, 1.60 N, 4.20 mmol) was dropwise added over a period of 5 minutes, and then the mixture was slowly heated to room temperature. After stirring for 2 hours at room temperature, the reaction solution was slowly added to an
- 10 ether slurry of 4.00 ml of titanium tetrachloride (heptane solution, 0.5 M, 2.00 mmol) having been cooled to  $-78^{\circ}\text{C}$ . After the addition, the mixture was slowly heated to room temperature. The resulting dark red slurry was filtered, and the filtrate was vacuum
- 15 concentrated. Then, 5 ml of ether and 30 ml of hexane were added, and the solids precipitated were collected and washed with hexane. The resulting solids were vacuum dried to obtain 0.530 g (yield: 40 %) of a reddish brown compound represented by the following formula (4). The
- 20 FD-mass spectrometry of the compound (4) resulted in 658 ( $\text{M}^+$ ).



(4)

Synthesis Example 5

In a 200 ml reactor thoroughly purged with nitrogen, 100 ml of toluene, 3.19 g (8.0 mmol) of 1H,1H-perfluorooctylamine, 1.43 g (8.0 mmol) of 3-t-butylsalicylaldehyde and a small amount of p-toluenesulfonic acid as a catalyst were placed, and they were heated and refluxed with stirring for 14 hours. The reaction solution was allowed to stand for cooling to room temperature, then filtered to remove the catalyst and vacuum concentrated, to obtain 4.04 g (yield: 90 %) of yellow solids represented by the following formula (e).

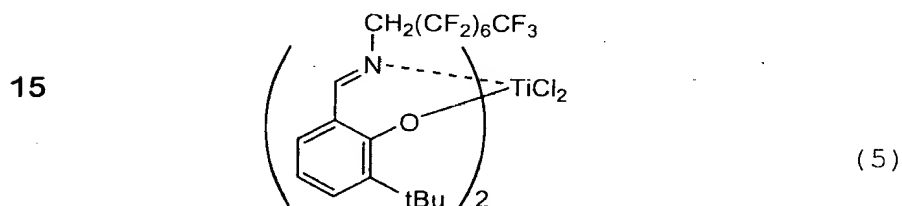


(e)

In a 30 ml reactor thoroughly purged with nitrogen, 1.12 g (2.00 mmol) of the compound (e) obtained above and 30 ml of anhydrous diethyl ether were placed, and the solution was cooled to  $-78^{\circ}C$  and stirred. To the solution, 1.31 ml of n-butyllithium (n-hexane solution, 1.60 N, 2.10 mmol) was dropwise added over a period of 5 minutes, and then the mixture was slowly heated to room temperature. After stirring for 2 hours at room



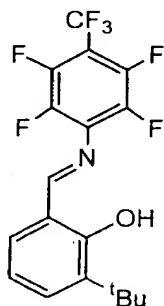
temperature, the reaction solution was slowly added to an ether slurry of 2.00 ml of titanium tetrachloride (heptane solution, 0.5 M, 1.00 mmol) having been cooled to -78°C. After the addition, the mixture was slowly heated to room temperature. The resulting dark red slurry was filtered, and the filtrate was vacuum concentrated. Then, 3 ml of ether and 20 ml of hexane were added, and the solids precipitated were collected and washed with hexane. The resulting solids were vacuum dried to obtain 0.183 g (yield: 15 %) of a reddish brown compound represented by the following formula (5). The FD-mass spectrometry of the compound (5) resulted in 1234 (M+).



#### Synthesis Example 6

In a 200 ml reactor thoroughly purged with nitrogen, 100 ml of toluene, 4.66 g (20.0 mmol) of 4-trifluoromethyl-2,3,5,6-tetrafluoroaniline, 1.78 g (10.0 mmol) of 3-t-butylsalicylaldehyde and a small amount of p-toluenesulfonic acid as a catalyst were placed, and they were heated and refluxed with stirring for 53 hours. The starting material was confirmed by the GC analysis,

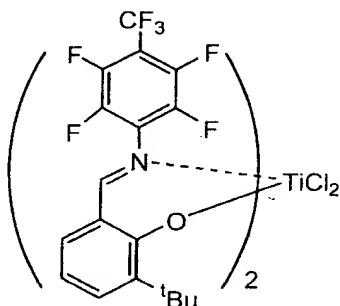
so that 2.33 g (10.0 mmol) of 2,3,5,6-tetrafluoro-4-trifluoromethylaniline was further added, and the mixture was heated and refluxed with stirring for 7 hours. The reaction solution was allowed to stand for cooling to room temperature, then filtered to remove the catalyst and vacuum concentrated. The residue was purified by a silica gel column to obtain 2.53 g (yield: 64 %) of light yellow solids represented by the following formula (f).



(f)

In a 100 ml reactor thoroughly purged with argon, 0.15 g (3.80 mmol) of sodium hydride was placed and washed twice with 10 ml of hexane. Then, 30 ml of diethyl ether was added to give a suspension. With stirring the suspension at room temperature, 20 ml of a diethyl ether solution containing the compound (f) obtained above was dropwise added over a period of 20 minutes, followed by further stirring for 2 hours. The solution was cooled to -78°C, and thereto was dropwise added 3.75 ml of titanium tetrachloride (heptane solution, 0.5 M, 1.88 mmol) over a period of 5 minutes. After the

dropwise addition was completed, the reaction solution was slowly heated to room temperature. After the solution was further stirred for 12 hours at room temperature, the resulting dark red slurry was filtered, and the filtrate was vacuum concentrated. Then, ether was added, and the solids precipitated were collected and vacuum dried to obtain 0.76 g (yield: 45 %) of a reddish brown powder represented by the following formula (6). The FD-mass spectrometry of the compound (6) resulted in 902 (M+).



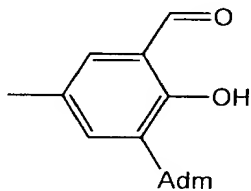
(6)

#### Synthesis Example 7

In a 200 ml reactor thoroughly purged with nitrogen, 16.2 ml of ethylmagnesium bromide (ether solution, 3M, 48.6 mmol) and 50 ml of anhydrous tetrahydrofuran were placed. Then, a solution of 11.2 g (46.2 mmol) of 2-(1-adamantyl)-4-methylphenol in 50 ml of anhydrous tetrahydrofuran was dropwise added over a period of 20 minutes with ice cooling. After the dropwise addition was completed, the reaction solution was stirred at room

- temperature. To the solution, 300 ml of toluene was added, and the mixture was heated with stirring to distill off the tetrahydrofuran and the diethyl ether. After cooling to room temperature, 3.80 g (127 mmol) of
- 5 paraformaldehyde and 7.1 g (70.2 mmol) of triethylamine were added, and the mixture was heated with stirring at 80 to 90 °C for 20 minutes. The resulting solution was cooled to room temperature, and thereto was added 200 ml of 10% hydrochloric acid with ice cooling. Then, 300 ml
- 10 of diethyl ether was added to perform phase separation, and the organic layer was washed twice with 200 ml of water and then with a sodium hydrogencarbonate aqueous solution. The resulting solution was dried over anhydrous sodium sulfate and then vacuum concentrated.
- 15 The resulting crystals were vacuum dried to obtain 10.5 g (yield: 84 %) of a yellow compound represented by the following formula (g) (wherein Adm denotes an adamantyl group).

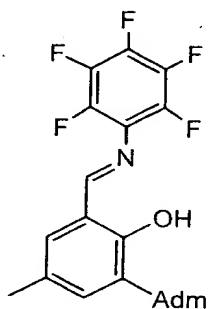
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(g)

- In a 100 ml reactor thoroughly purged with nitrogen, 80 ml of toluene, 2.75 g (15.0 mmol) of
- 25 pentafluoroaniline, 4.07 g (99.7 %, 15.0 mmol) of the

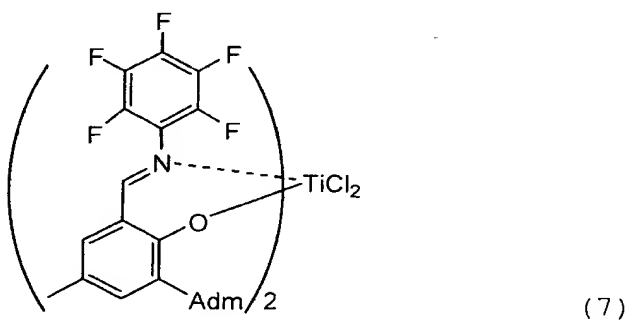
compound (g) obtained above and a small amount of p-toluenesulfonic acid as a catalyst were placed, and they were heated and refluxed with stirring for five and half hours. After the reaction solution was allowed to stand for cooling, the solvent was distilled off under reduced pressure. Then, 50 ml of methanol was added, and the mixture was stirred and filtered. The resulting solids were vacuum dried to obtain 4.38 g (yield: 67 %) of yellow solids represented by the following formula (g').



(g')

In a 50 ml reactor thoroughly purged with nitrogen, 1.35 g (3.00 mmol) of the compound (g') obtained above and 20 ml of anhydrous diethyl ether were placed, and the solution was cooled to  $-78^{\circ}\text{C}$  and stirred. To the solution, 1.89 ml of n-butyllithium (n-hexane solution, 1.59 N, 3.00 mmol) was dropwise added over a period of 5 minutes, and the mixture was stirred for 2 hours and then slowly heated to room temperature. After stirring for 3 hours at room temperature, the solution was dropwise added to 20 ml of a tetrahydrofuran solution of 3.00 ml

of titanium tetrachloride (heptane solution, 0.5 M, 1.50 mmol) having been cooled to  $-78^{\circ}\text{C}$ . After the dropwise addition was completed, the mixture was slowly heated to room temperature and stirred for 12 hours at room temperature. Then, the solvent was distilled off under reduced pressure. To the resulting solids, 40 ml of methylene chloride was added. The mixture was stirred and filtered, and the filtrate was vacuum concentrated. The solids precipitated were reprecipitated with hexane, and the resulting solids were vacuum dried to obtain 0.334 g (yield: 23 %) of a brown compound represented by the following formula (7). The FD-mass spectrometry of the compound (7) resulted in 986 ( $\text{M}^+$ ).



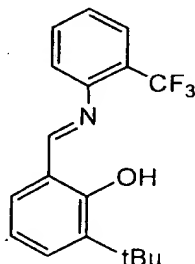
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#### Synthesis Example 8

In a 200 ml reactor thoroughly purged with nitrogen, 100 ml of toluene, 4.19 g (26.0 mmol) of o-trifluoromethylaniline, 2.32 g (13.0 mmol) of 3-t-butylsalicylaldehyde and a small amount of p-

25

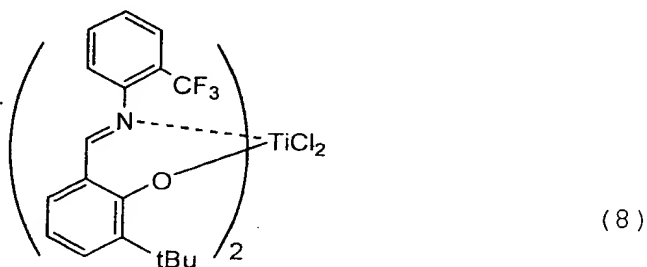
toluenesulfonic acid as a catalyst were placed, and they were heated and refluxed with stirring for 5 hours. The reaction solution was allowed to stand for cooling to room temperature, then filtered to remove the catalyst and vacuum concentrated. The residue was purified by a silica gel column to obtain 3.20 g (yield: 77 %) of a yellow oil represented by the following formula (h).



(h)

In a 30 ml reactor thoroughly purged with nitrogen, 1.29 g (4.00 mmol) of the compound (h) obtained above and 30 ml of anhydrous diethyl ether were placed, and the solution was cooled to  $-78^{\circ}\text{C}$  and stirred. To the solution, 2.63 ml of n-butyllithium (n-hexane solution, 1.60 N, 4.20 mmol) was dropwise added over a period of 5 minutes, and then the mixture was slowly heated to room temperature. After stirring for 2 hours at room temperature, the reaction solution was slowly added to an ether slurry of 4.00 ml of titanium tetrachloride (heptane solution, 0.5 M, 2.00 mmol) having been cooled to  $-78^{\circ}\text{C}$ . After the addition, the mixture was slowly

heated to room temperature. The resulting dark red slurry was filtered, and the filtrate was vacuum concentrated. Then, 5 ml of ether and 30 ml of hexane were added, and the solids precipitated were collected and washed with hexane. The resulting solids were vacuum dried to obtain 0.80 g (yield: 53 %) of a reddish brown compound represented by the following formula (8). The FD-mass spectrometry of the compound (8) resulted in 758 (M+).



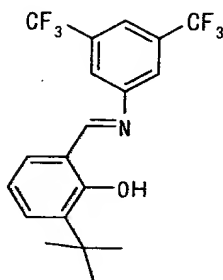
15 Synthesis Example 9

In a 100 ml reactor thoroughly purged with nitrogen, 55 ml of ethanol and 3.44 g (15.0 mmol) of 3,5-ditrifluoromethylaniline were placed, and they were stirred. To the solution, 1.79 g (10.0 mmol) of 3-t-butylsalicylaldehyde was added, followed by stirring for 19 hours at room temperature. Then, 6.00 g of molecular sieves 4A were added, and the mixture was heated and refluxed with stirring for 5 hours. The solids were removed by filtration, and the solution was concentrated.

25 The resulting solids were purified by a silica gel column



to obtain 0.92 g (yield: 72 %) of yellow solids represented by the following formula (i).



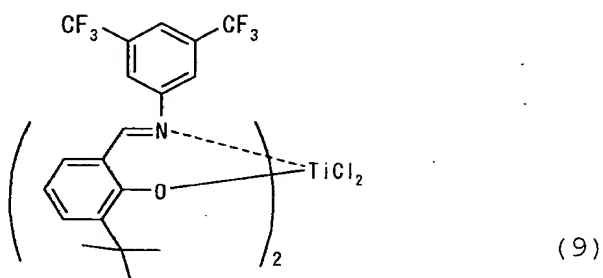
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(i)

In a 30 ml reactor thoroughly purged with nitrogen, 0.779 g (2.00 mmol) of the compound (i) obtained above and 20 ml of anhydrous diethyl ether were placed, and the solution was cooled to  $-78^{\circ}\text{C}$  and stirred. To the solution, 1.43 ml of n-butyllithium (n-hexane solution, 1.54 N, 2.20 mmol) was dropwise added over a period of 5 minutes, followed by stirring for 3 hours. Thereafter, the mixture was stirred for 5 hours with slowly heating to room temperature and then slowly added to an ether slurry of 2.00 ml of titanium tetrachloride (heptane solution, 0.5 M, 1.00 mmol) having been cooled to  $-78^{\circ}\text{C}$ . After the addition, the mixture was slowly heated to room temperature. The resulting dark red slurry was filtered, and the solution was concentrated to 10 ml. The crystals obtained by filtration were washed with hexane and vacuum dried to obtain 0.269 g (yield: 30.1 %) of a reddish

brown compound represented by the following formula (9).  
The FD-mass spectrometry of the compound (9) resulted in  
894 (M+).

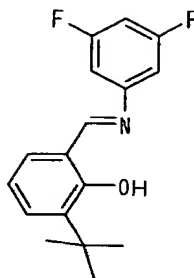
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#### 10 Synthesis Example 10

In a 200 ml reactor thoroughly purged with nitrogen,  
100 ml of toluene and 3.36 g (26.0 mmol) of 3,5-  
difluoroaniline were placed, followed by stirring. To  
the solution, 2.32 g (13.0 mmol) of 3-t-

- 15 butylsalicylaldehyde and a small amount of p-  
toluenesulfonic acid were added, and the mixture was  
heated and refluxed with stirring for 6.5 hours. The  
solids were removed by filtration, and the solution was  
concentrated. The concentrate was purified by a silica  
20 gel column to obtain 3.32 g (yield: 89 %) of yellow  
solids represented by the following formula (j).



(j)

In a 50 ml reactor thoroughly purged with nitrogen,

5 1.16 g (4.00 mmol) of the compound (j) obtained above and 30 ml of anhydrous diethyl ether were placed, and the solution was cooled to  $-78^{\circ}\text{C}$  and stirred. To the solution, 2.63 ml of n-butyllithium (n-hexane solution, 1.60 N, 4.20 mmol) was dropwise added over a period of 5

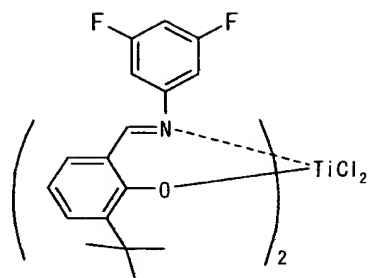
10 minutes. Thereafter, the mixture was stirred for 12 hours with slowly heating to room temperature and then slowly added to an ether slurry of 4.00 ml of titanium tetrachloride (heptane solution, 0.5 M, 2.00 mmol) having been cooled to  $-78^{\circ}\text{C}$ . After the addition, the mixture

15 was slowly heated to room temperature. The resulting dark red slurry was filtered, and the solution was concentrated. The crystals obtained by filtration were washed with hexane and vacuum dried to obtain 0.958 g (yield: 69 %) of a reddish brown compound represented by

20 the following formula (10). The FD-mass spectrometry of the compound (10) resulted in 694 ( $\text{M}^+$ ).

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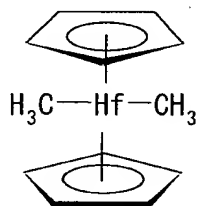


(10)

Synthesis Example 11

In a 100 ml reactor thoroughly purged with nitrogen, 2.00 g (5.27 mmol) of hafnocene dichloride and 40 ml of anhydrous diethyl ether were placed, and the solution was cooled to 0°C and stirred. To the solution, 9.6 ml of methyllithium (ether solution, 1.14 N, 10.9 mmol) was dropwise added over a period of 45 minutes, followed by stirring for 2 hours. Then, the mixture was slowly heated to 0°C. After stirring for 30 minutes at 0°C, insolubles were removed by filtration. The filtrate was concentrated, and to the concentrate was added 10 ml of ether to give a suspension. Then, insolubles were removed again, and the solution was vacuum concentrated to obtain 1.79 g (quantitative yield) of a light yellow compound represented by the following formula (11).

25



(11)

Example 1

- In a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of toluene was placed, and a mixed gas of ethylene (50 l/hr) and propylene (150 l/hr) was fed to saturate the liquid phase and the gas phase. Thereafter, 1.25 mmol (in terms of aluminum atom) of methylaluminoxane and then 0.005 mmol of the titanium compound (1) were added to initiate polymerization.
- After the polymerization was conducted at 50°C for 5 minutes, a small amount of isobutanol was added to terminate the polymerization.

- The resulting polymer solution was introduced into 1.5 liters of methanol containing a small amount of hydrochloric acid to precipitate a polymer. The polymer precipitated was washed with methanol and then vacuum dried at 130°C for 10 hours. Thus, 0.794 g of an ethylene/propylene copolymer was obtained. The polymerization activity was 1.91 kg/hr based on 1 mmol of titanium. The propylene content as measured by IR was 13.3 % by mol, the molecular weight ( $M_n$ ) as measured by GPC was 159,000, and the molecular weight distribution ( $M_w/M_n$ ) was 1.09.

25 Example 2

Polymerization was conducted in the same manner as in Example 1, except that the polymerization time was changed to 10 minutes. Thus, 1.318 g of an ethylene/propylene copolymer was obtained. The polymerization activity was 1.58 kg/hr based on 1 mmol of titanium. The propylene content as measured by IR was 15.0 % by mol, the molecular weight (Mn) as measured by GPC was 233,000, and the molecular weight distribution (Mw/Mn) was 1.16.

10

Example 3

Polymerization was conducted in the same manner as in Example 1, except that the polymerization time was changed to 20 minutes. Thus, 2.225 g of an ethylene/propylene copolymer was obtained. The polymerization activity was 1.34 kg/hr based on 1 mmol of titanium. The propylene content as measured by IR was 15.4 % by mol, the molecular weight (Mn) as measured by GPC was 345,000, and the molecular weight distribution (Mw/Mn) was 1.29.

15  
20Example 4

In a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of toluene was placed, and ethylene was fed to saturate the liquid phase and the gas phase.

25

Thereafter, 1.25 mmol (in terms of aluminum atom) of methylaluminumoxane and then 0.0005 mmol of the titanium compound (1) were added to initiate polymerization. After the reaction was conducted at 25°C for 0.5 minute in an ethylene gas atmosphere at ordinary pressure, a small amount of methanol was added to terminate the polymerization. After the polymerization was completed, the reaction product was introduced into a large amount of methanol to precipitate the whole polymer. To the polymer, hydrochloric acid was added, followed by filtration over a glass filter. The resulting polymer was vacuum dried at 80°C for 10 hours to obtain 0.149 g of polyethylene (PE). The polymerization activity was 35.8 kg based on 1 mmol of titanium. The number-average molecular weight ( $M_n$ ) and the weight-average molecular weight ( $M_w$ ) of the resulting polyethylene were 191,000 and 219,000, respectively, and  $M_w/M_n$  was 1.15.

#### Examples 5 - 22

Polymerization was conducted in the same manner as described above, except that the catalytic amount, the polymerization time and the polymerization temperature were changed as shown in Table 1. The polymerization activity, molecular weight of the resulting polymer and

molecular weight distribution thereof are set forth in Table 1.

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Table 1

| Example | Titanium Compound amount |        | Amount of MAO (mmol) | Temp (°C) | Time (min.) | Monomer            | yield (g) | Activity (kg/mmol-Ti·h) | Mn ( $\times 10^4$ ) | Mw ( $\times 10^4$ ) | Mw/Mn |
|---------|--------------------------|--------|----------------------|-----------|-------------|--------------------|-----------|-------------------------|----------------------|----------------------|-------|
| 1       | 1                        | 0.005  | 1.25                 | 50        | 5           | Ethylene/propylene | 0.794     | 1.90                    | 15.9                 | 17.4                 | 1.09  |
| 2       | 1                        | 0.005  | 1.25                 | 50        | 10          | Ethylene/propylene | 1.318     | 1.58                    | 23.3                 | 27.1                 | 1.16  |
| 3       | 1                        | 0.005  | 1.25                 | 50        | 20          | Ethylene/propylene | 2.225     | 1.34                    | 34.5                 | 44.4                 | 1.29  |
| 4       | 1                        | 0.0005 | 1.25                 | 25        | 0.5         | Ethylene           | 0.149     | 35.8                    | 19.1                 | 21.9                 | 1.15  |
| 5       | 1                        | 0.0005 | 1.25                 | 50        | 0.5         | Ethylene           | 0.172     | 41.3                    | 25.7                 | 27.9                 | 1.08  |
| 6       | 1                        | 0.001  | 1.25                 | 75        | 0.5         | Ethylene           | 0.247     | 29.6                    | 21.4                 | 23.3                 | 1.09  |
| 7       | 1                        | 0.0005 | 1.25                 | 25        | 1           | Ethylene           | 0.283     | 34.0                    | 41.2                 | 46.4                 | 1.13  |
| 8       | 1                        | 0.0005 | 1.25                 | 50        | 1           | Ethylene           | 0.302     | 36.2                    | 42.4                 | 47.7                 | 1.13  |
| 9       | 1                        | 0.001  | 1.25                 | 75        | 1           | Ethylene           | 0.453     | 27.2                    | 32.9                 | 37.7                 | 1.15  |
| 10      | 2                        | 0.005  | 1.25                 | 25        | 2           | Ethylene           | 0.340     | 2.04                    | 5.64                 | 6.02                 | 1.07  |
| 11      | 2                        | 0.005  | 1.25                 | 50        | 2           | Ethylene           | 0.435     | 2.61                    | 6.95                 | 7.44                 | 1.07  |
| 12      | 2                        | 0.005  | 1.25                 | 75        | 2           | Ethylene           | 0.448     | 2.69                    | 7.72                 | 8.44                 | 1.09  |
| 13      | 3                        | 0.005  | 1.25                 | 25        | 5           | Ethylene           | 0.186     | 0.45                    | 3.99                 | 4.26                 | 1.07  |
| 14      | 3                        | 0.005  | 1.25                 | 50        | 5           | Ethylene           | 0.315     | 0.76                    | 5.82                 | 6.14                 | 1.06  |
| 15      | 3                        | 0.005  | 1.25                 | 75        | 5           | Ethylene           | 0.215     | 0.52                    | 6.14                 | 7.00                 | 1.14  |
| 16      | 4                        | 0.005  | 1.25                 | 25        | 30          | Ethylene           | 0.149     | 0.06                    | 2.38                 | 2.89                 | 1.22  |
| 17      | 5                        | 0.002  | 1.25                 | 25        | 5           | Ethylene           | 0.184     | 1.10                    | 6.08                 | 8.33                 | 1.37  |
| 18      | 6                        | 0.0005 | 1.25                 | 50        | 0.5         | Ethylene           | 0.271     | 65.0                    | 24.7                 | 33.2                 | 1.34  |
| 19      | 7                        | 0.0005 | 1.25                 | 25        | 1           | Ethylene           | 0.133     | 16.0                    | 19.9                 | 24.0                 | 1.21  |
| 20      | 7                        | 0.0005 | 1.25                 | 50        | 1           | Ethylene           | 0.171     | 20.6                    | 22.6                 | 28.1                 | 1.24  |
| 21      | 7                        | 0.0005 | 1.25                 | 75        | 1           | Ethylene           | 0.170     | 20.4                    | 18.2                 | 24.0                 | 1.31  |
| 22      | 8                        | 0.005  | 1.25                 | 50        | 15          | Ethylene           | 0.079     | 0.063                   | 2.00                 | 2.28                 | 1.14  |

Example 23

In a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of toluene was placed, and propylene was fed to saturate the liquid phase and the gas phase.

- 5 Thereafter, 2.50 mmol (in terms of aluminum atom) of methylaluminoxane and then 0.01 mmol of the titanium compound (1) were added to initiate polymerization. After the reaction was conducted at 25°C for 30 minutes, a small amount of isobutanol was added to terminate the
- 10 polymerization. After the polymerization was completed, the reaction product was introduced into methanol containing a small amount of hydrochloric acid to precipitate the whole polymer, followed by filtration over a glass filter. The resulting polymer was vacuum
- 15 dried at 80°C for 10 hours to obtain 0.4 mg of polypropylene (PP). The number-average molecular weight ( $M_n$ , in terms of PP) and the weight-average molecular weight ( $M_w$ , in terms of PP) of the resulting PP were 4,200 and 4,400, respectively, and  $M_w/M_n$  was 1.05.

20

Example 24

- Polypropylene (PP) of 96 mg was obtained in the same manner as in Example 23, except that the polymerization time was prolonged to 3 hours. The number-average
- 25 molecular weight ( $M_n$ , in terms of PP) and the weight-

average molecular weight ( $M_w$ , in terms of PP) of the resulting PP were 20,500 and 22,400, respectively, and  $M_w/M_n$  was 1.09.

5 Example 25

Polypropylene (PP) of 180 mg was obtained in the same manner as in Example 23, except that the polymerization time was prolonged to 5 hours. The number-average molecular weight ( $M_n$ ) and the weight-average molecular weight ( $M_w$ ) of the resulting PP were 28,500 and 31,600, respectively, and  $M_w/M_n$  was 1.11. Measurement of the melting point of the polymer by DSC resulted in 139°C.

15 Example 26

Polypropylene (PP) of 376 mg was obtained in the same manner as in Example 23, except that the titanium compound (6) was used instead of the titanium compound (1) and the polymerization time was prolonged to 5 hours. The number-average molecular weight ( $M_n$ , in terms of PP) and the weight-average molecular weight ( $M_w$ , in terms of PP) of the resulting PP were 52,000 and 66,200, respectively, and  $M_w/M_n$  was 1.27.

25 Example 27

In a 1 liter stainless steel autoclave thoroughly purged with nitrogen, 380 ml of heptene was placed, and propylene was fed at 25°C to saturate the liquid phase and the gas phase. Thereafter, 2.5 mmol (in terms of  
5 aluminum atom) of methylaluminoxane and 0.01 mmol of the titanium compound (1) were added, and polymerization was conducted for 3 hours at a propylene pressure of 5 kg/cm<sup>2</sup>-G.

To the resulting polymer suspension, 1.5 liters of  
10 methanol containing a small amount of hydrochloric acid were added to precipitate a polymer. The polymer was filtered over a glass filter to remove the solvent, then washed with methanol and vacuum dried at 80°C for 10 hours. Thus, 0.691 g of polypropylene was obtained. Mn  
15 (in terms of PP) as measured by GPC was 78,000, Mw/Mn was 1.15, and Tm was 134.8°C.

#### Example 28

Polymerization was conducted in the same manner as  
20 described above, except that the polymerization time was changed to 5 hours. Thus, 1.125 g of polypropylene was obtained. Mn (in terms of PP) as measured by GPC was 138,000, Mw/Mn was 1.11, and Tm was 130.5°C.

#### 25 Example 29

In a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of toluene was placed, and a mixed gas of ethylene and butene (ethylene: 40 l/hr, butene: 60 l/hr) was blown into the autoclave for 20 minutes.

- 5 Thereafter, 1.25 mmol (in terms of aluminum atom) of methylaluminoxane and then 0.001 mmol of the titanium compound (1) were added to initiate polymerization. After the reaction was conducted at 25°C for 5 minutes with blowing the mixed gas into the autoclave, a small
- 10 amount of methanol was added to terminate the polymerization. After the polymerization was completed, the reaction product was introduced into methanol containing a small amount of hydrochloric acid dissolved therein to precipitate a polymer, followed by filtration
- 15 over a glass filter. The resulting polymer was vacuum dried at 130°C for 10 hours to obtain 0.056 g of an ethylene/butene copolymer. The polymerization activity was 0.67 kg based on 1 mmol of titanium. The number-average molecular weight ( $M_n$ ) of the polymer was 49,100,
- 20 the molecular weight distribution ( $M_w/M_n$ ) was 1.14, and the butene content was 8.4 % by mol.

#### Examples 30 - 33

- Polymerization was conducted in the same manner as
- 25 in Example 29, except that the feed rates of ethylene and

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butene, the polymerization time and the polymerization temperature were changed as shown in Table 2. The polymerization activity, molecular weight of the resulting polymer and molecular weight distribution are set forth in Table 2.

Table 2

| Ex. | Titanium compound amount (mmol) |       | Time (min) | Ethylene/butene feed rate (L/h) | Yield (g) | Activity (kg/mmol - Ti·h) | Mn ( $\times 10^4$ ) | Mw ( $\times 10^4$ ) | Mw/Mn | Butene content (mol %) |
|-----|---------------------------------|-------|------------|---------------------------------|-----------|---------------------------|----------------------|----------------------|-------|------------------------|
| 29  | 1                               | 0.001 | 5          | 40/60                           | 0.056     | 0.67                      | 4.91                 | 5.61                 | 1.14  | 8.4                    |
| 30  | 1                               | 0.001 | 10         | 40/60                           | 0.087     | 0.52                      | 6.90                 | 7.82                 | 1.13  | 10.5                   |
| 31  | 1                               | 0.001 | 5          | 70/30                           | 0.258     | 3.10                      | 16.1                 | 18.9                 | 1.17  | 3.7                    |
| 32  | 1                               | 0.001 | 10         | 70/30                           | 0.456     | 2.74                      | 22.4                 | 27.9                 | 1.24  | 3.7                    |
| 33  | 1                               | 0.001 | 5          | 50/50                           | 0.088     | 1.06                      | 7.31                 | 8.28                 | 1.13  | 5.9                    |

#### 10 Example 34

In a 500 ml glass autoclave thoroughly purged with nitrogen, 200 ml of dry toluene was placed, and 1-butene was passed through the autoclave for 40 minutes at a rate of 100 l/hr. Then, the polymerization temperature was maintained at 25°C, and 5.00 mmol (in terms of aluminum) of methylaluminoxane was added. Subsequently, 0.05 mmol of the titanium compound (1) was added, and a mixed gas of ethylene and 1-butene (ethylene: 20 l/hr, 1-butene: 80 l/hr) was passed through, followed by stirring for 60 minutes. Then, 20 ml of isobutyl alcohol was added to

terminate the reaction. Subsequently, 10 ml of a 1N hydrochloric acid aqueous solution was added, followed by stirring for 30 minutes in a stream of nitrogen. The polymer solution was poured into 1.5 liters of methanol to precipitate a polymer, followed by stirring for one night by a magnetic stirrer. The polymer was filtered over a glass filter and dried at 80°C for 10 hours under reduced pressure to obtain 1.79 g of an ethylene/1-butene copolymer. As a result of GPC analysis, the number-average molecular weight was 29,000, and Mw/Mn was 1.15 (in terms of polyethylene). As a result of IR analysis, the 1-butene content was 22.8 % by mol.

#### Example 35

In a 500 ml glass autoclave thoroughly purged with nitrogen, 200 ml of dry toluene was placed, and 1-butene was passed through the autoclave for 40 minutes at a rate of 100 l/hr. Then, the polymerization temperature was maintained at 25°C, and 5.00 mmol (in terms of aluminum) of methylaluminoxane was added. Subsequently, 0.05 mmol of a catalyst was added, and a mixed gas of ethylene and 1-butene (ethylene: 40 l/hr, 1-butene: 60 l/hr) was passed through, followed by stirring for 30 minutes. Then, 20 ml of isobutyl alcohol was added to terminate the reaction. Subsequently, 10 ml of a 1N hydrochloric

acid aqueous solution was added, followed by stirring for 30 minutes in a stream of nitrogen. The polymer solution was poured into 1.5 liters of methanol to precipitate a polymer, followed by stirring for one night by a magnetic stirrer. The polymer was filtered over a glass filter and dried at 80°C for 10 hours under reduced pressure to obtain 5.15 g of an ethylene/1-butene copolymer. As a result of GPC analysis, the number-average molecular weight was 73,000, and Mw/Mn was 1.16 (in terms of polyethylene). As a result of IR analysis, the 1-butene content was 14.5 % by mol.

#### Example 36

In a 500 ml glass autoclave thoroughly purged with nitrogen, 200 ml of dry toluene was placed, and 1-butene was passed through the autoclave for 40 minutes at a rate of 100 l/hr. Then, the polymerization temperature was maintained at 25°C, and 5.00 mmol (in terms of aluminum) of methylaluminoxane was added. Subsequently, 0.05 mmol of a catalyst was added, and a mixed gas of ethylene and 1-butene (ethylene: 60 l/hr, 1-butene: 40 l/hr) was passed through, followed by stirring for 10 minutes. Then, 20 ml of isobutyl alcohol was added to terminate the reaction. Subsequently, 10 ml of a 1N hydrochloric acid aqueous solution was added, followed by stirring for



30 minutes in a stream of nitrogen. The polymer solution was poured into 1.5 liters of methanol to precipitate a polymer, followed by stirring for one night by a magnetic stirrer. The polymer was filtered over a glass filter  
5 and dried at 80°C for 10 hours under reduced pressure to obtain 2.38 g of an ethylene/1-butene copolymer. As a result of GPC analysis, the number-average molecular weight was 38,800, and Mw/Mn was 1.18 (in terms of polyethylene). As a result of IR analysis, the 1-butene  
10 content was 11.3 % by mol.

#### Example 37

In a 500 ml glass autoclave thoroughly purged with nitrogen, 200 ml of toluene and 50 ml of 1-hexene were  
15 placed, and ethylene was fed to saturate the liquid phase and the gas phase with stirring. Thereafter, 1.25 mmol (in terms of aluminum atom) of methylaluminumoxane and then 0.0025 mmol of the titanium compound (1) were added to initiate polymerization. After the reaction was  
20 conducted at 25°C for 5 minutes with blowing ethylene into the autoclave, a small amount of methanol was added to terminate the polymerization. After the polymerization was completed, the reaction product was introduced into methanol containing a small amount of  
25 hydrochloric acid dissolved therein to precipitate a

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polymer, followed by filtration over a glass filter. The polymer was vacuum dried at 130°C for 10 hours to obtain 0.304 g of an ethylene/hexene copolymer. The polymerization activity was 1.46 kg based on 1 mmol of titanium. The number-average molecular weight (Mn) of the resulting polymer was 95,600, Mw/Mn was 1.17, and the hexene content was 2.7 % by mol.

#### Example 38

An ethylene/hexene copolymer of 0.241 g was obtained in the same manner as in Example 37, except that the amount of the titanium compound (1) was changed to 0.001 mmol, the amount of toluene was changed to 225 ml, and the amount of 1-hexene was changed to 25 ml. The polymerization activity was 2.89 kg based on 1 mmol of titanium. The number-average molecular weight (Mn) of the resulting polymer was 152,000, Mw/Mn was 1.22, and the hexene content was 1.7 % by mol.

#### Example 39

In a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of toluene was placed, and ethylene was fed to saturate the liquid phase and the gas phase temporarily. Then, only the gas phase was purged with nitrogen. Thereafter, 2.5 mmol (in terms of aluminum

atom) of methylaluminoxane and then 0.01 mmol of the titanium compound (1) were added to initiate polymerization. After the reaction was conducted at 25°C for 5 minutes, a small amount of methanol was added to terminate the polymerization. Then, hydrochloric acid and a large amount of methanol was added to precipitate a polymer. The polymer was filtered, washed with methanol and vacuum dried to obtain 0.800 g of polyethylene (PE). The number-average molecular weight ( $M_n$ , in terms of PP) of the resulting polyethylene was 115,000, and  $M_w/M_n$  was 1.10. Conversion from the polymer yield showed that ethylene in the system was quantitatively consumed.

#### Example 40

In Example 39, after the reaction was conducted at 25°C for 5 minutes to completely consume ethylene, a propylene gas (30 l/hr) was blown into the system to perform reaction for 20 minutes. Then, feeding of propylene was stopped, followed by further reaction for 280 minutes. Then, a small amount of methanol was added to terminate the reaction, and the reaction product was introduced into 1 liter of methanol containing a small amount of hydrochloric acid to precipitate a polymer. The polymer was filtered, washed with methanol and vacuum dried at 130°C for 10 hours to obtain 1.135 g of a

polymer. The number-average molecular weight ( $M_n$ , in terms of PP) of the resulting polymer was 136,000,  $M_w/M_n$  was 1.15, and the propylene content was 14.6 % by mol.

In comparison with the polyethylene prepolymer  
5 prepared in Example 39, this polymer was increased in the molecular weight with keeping a narrow molecular weight distribution, and propylene was incorporated into the polymer. From this, it can be seen that a polyethylene-polypropylene diblock copolymer was quantitatively  
10 produced.

#### Example 41

In Example 39, after the reaction of ethylene was conducted at 25°C for 5 minutes, an ethylene gas (25  
15 l/hr) and a propylene gas (75 l/hr) were blown into the system to perform reaction for 3 minutes. Then, feeding of the mixed gas was stopped, followed by further reaction for 3 minutes. Then, a small amount of methanol was added to terminate the reaction, and the reaction  
20 product was introduced into 1 liter of methanol containing a small amount of hydrochloric acid to precipitate a polymer. The polymer was filtered, washed with methanol and vacuum dried at 130°C for 10 hours to obtain 1.700 g of a polymer. The number-average  
25 molecular weight ( $M_n$ , in terms of PP) of the resulting

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polymer was 211,000, the molecular weight distribution (Mw/Mn) was 1.16, and the propylene content was 6.4 % by mol.

In comparison with the polyethylene prepolymer prepared in Example 39, this polymer was increased in the molecular weight with keeping a narrow molecular weight distribution, and propylene was incorporated into the polymer. From this, it can be seen that a polyethylene-ethylene/propylene diblock copolymer was quantitatively produced. The propylene content in the second block component (ethylene/propylene copolymer portion), as calculated from the molecular weight and the propylene content in the whole polymer, was 14.6 % by mol.

Example 42

In Example 39, after the reaction of ethylene was conducted at 25°C for 5 minutes, an ethylene gas (25 l/hr) and a propylene gas (75 l/hr) were blown into the system to perform reaction for 3 minutes. Then, feeding of the mixed gas was stopped, followed by further reaction for 3 minutes. Subsequently, propylene (30 l/hr) was blown into the system for 20 minutes to perform reaction. Then, feeding of propylene was stopped, followed by further reaction for 280 minutes. Then, a small amount of methanol was added to terminate the

reaction, and the reaction product was introduced into 1 liter of methanol containing a small amount of hydrochloric acid to precipitate a polymer. The polymer was filtered, washed with methanol and vacuum dried at 130°C for 10 hours to obtain 1.814 g of a polymer. The number-average molecular weight ( $M_n$ , in terms of PP) of the resulting polymer was 235,000, the molecular weight distribution ( $M_w/M_n$ ) was 1.15, and the propylene content was 14.1 % by mol.

In comparison with the polyethylene-ethylene/propylene diblock copolymer prepolymer prepared in Example 41, this polymer was increased in the molecular weight with keeping a narrow molecular weight distribution, and propylene was incorporated into the polymer. From this, it can be seen that a polyethylene-ethylene/propylene copolymer-polypropylene triblock copolymer was quantitatively produced. The increase of the propylene content agreed with the value calculated on the assumption that the third block component introduced in this example was polypropylene.

#### Example 43

In Example 39, after the reaction of ethylene was conducted at 25°C for 5 minutes, an ethylene gas (25 l/hr) and a propylene gas (75 l/hr) were blown into the

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system to perform reaction for 3 minutes. Then, feeding of the mixed gas was stopped, followed by further reaction for 3 minutes. Subsequently, an ethylene gas (100 l/hr) was blown into the system to perform reaction for 1 minute. Then, a small amount of methanol was added to terminate the reaction, and the reaction product was introduced into 1 liter of methanol containing a small amount of hydrochloric acid, followed by stirring, to precipitate a polymer. The polymer was filtered, washed with methanol and vacuum dried at 130°C for 10 hours to obtain 1.998 g of a polyethylene-ethylene/propylene copolymer-LLDPE block polymer. The number-average molecular weight ( $M_n$ , in terms of PP) of the resulting polymer was 272,000,  $M_w/M_n$  was 1.13, and the propylene content was 6.6 % by mol.

In comparison with the polyethylene-ethylene/propylene diblock copolymer prepolymer prepared in Example 41, this polymer was increased in the molecular weight with keeping a narrow molecular weight distribution, and the ethylene content in the polymer was increased. From this, it can be seen that a polyethylene-ethylene/propylene copolymer-LLDPE triblock copolymer was quantitatively produced. The propylene content in the third block component (LLDPE portion), as

calculated from the molecular weight and the propylene content in the whole polymer, was 7.3 % by mol.

Example 44

- 5 Polymerization was conducted in the same manner as in Example 39, except that the catalytic amount was changed to 0.02 mmol. Thus, 0.800 g of polyethylene (PE) was obtained. The number-average molecular weight ( $M_n$ , in terms of PP) of the resulting polyethylene was 78,200, and the molecular weight distribution ( $M_w/M_n$ ) was 1.14.

- 10 In this example, after the reaction of ethylene was conducted at 25°C for 5 minutes, an ethylene gas (20 l/hr) and a butene gas (80 l/hr) were blown into the system to perform reaction for 3 minutes. Then, feeding of the mixed gas was stopped, followed by further reaction for 3 minutes. Then, a small amount of methanol was added to terminate the reaction, and the reaction product was introduced into 1 liter of methanol containing a small amount of hydrochloric acid, followed by stirring, to precipitate a polymer. The polymer was filtered, washed with methanol and vacuum dried at 130°C for 10 hours to obtain 1.416 g of a polyethylene-ethylene/butene copolymer block polymer. The number-average molecular weight ( $M_n$ , in terms of PP) of the resulting polymer was 120,600, the molecular weight



distribution (Mw/Mn) was 1.13, and the butene content in the whole polymer was 1.9 % by mol.

In comparison with the polyethylene prepolymer prepared in Example 39, this polymer was increased in the  
5 molecular weight with keeping a narrow molecular weight distribution, and butene was incorporated into the polymer. From this, it can be seen that a polyethylene-ethylene/LLDPE diblock copolymer was quantitatively produced. The butene content in the second block  
10 component (LLDPE portion), as calculated from the molecular weight and the butene content in the whole polymer, was 5.6 % by mol.

#### Example 45

15 In Example 39, after the reaction of ethylene was conducted at 25°C for 5 minutes, an ethylene gas (20 l/hr) and a butene gas (80 l/hr) were blown into the system to perform reaction for 3 minutes. Then, feeding of the mixed gas was stopped, followed by further  
20 reaction for 3 minutes. Subsequently, an ethylene gas (100 l/hr) was blown into the system to perform reaction for 1 minute. Then, a small amount of methanol was added to terminate the reaction, and the reaction product was introduced into 1 liter of methanol containing a small  
25 amount of hydrochloric acid, followed by stirring, to

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precipitate a polymer. The polymer was filtered, washed with methanol and vacuum dried at 130°C for 10 hours to obtain 1.921 g of a polyethylene-LLDPE-HDPE block polymer. The number-average molecular weight ( $M_n$ , in terms of PP) of the resulting polymer was 141,400, the molecular weight distribution ( $M_w/M_n$ ) was 1.14, and the butene content in the whole polymer was 2.0 % by mol.

In comparison with the polyethylene-LLDPE diblock copolymer prepolymer prepared in Example 44, this polymer was increased in the molecular weight with keeping a narrow molecular weight distribution, and the ethylene content in the polymer was changed. From this, it can be seen that a polyethylene-LLDPE-HDPE triblock copolymer was quantitatively produced. The butene content in the third block component (HDPE portion), as calculated from the molecular weight and the butene content in the whole polymer, was 2.6 % by mol.

#### Example 46

In a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of toluene was placed, and propylene was fed at 25°C to saturate the liquid phase and the gas phase. Thereafter, 2.5 mmol (in terms of aluminum atom) of methylaluminoxane and then 0.01 mmol of the titanium compound (1) were added to initiate polymerization.

After the reaction was conducted at 25°C for 180 minutes, a small amount of methanol was added to terminate the polymerization. Then, the reaction product was added to methanol containing a small amount of hydrochloric acid, followed by stirring, to precipitate a polymer. The polymer was filtered, washed with methanol and vacuum dried at 130°C for 8 hours to obtain 0.100 g of polypropylene. The number-average molecular weight ( $M_n$ , in terms of PP) of the resulting polymer was 17,200, and  $M_w/M_n$  was 1.15.

#### Example 47

In Example 46, after the reaction of propylene was conducted for 180 minutes, an ethylene gas (20 l/hr) was blown into the system to perform reaction for 3 minutes, and a small amount of methanol was added to terminate the reaction. Then, the reaction product was introduced into 1 liter of methanol containing a small amount of hydrochloric acid, followed by stirring, to precipitate a polymer. The polymer was filtered, washed with methanol and vacuum dried to obtain 0.481 g of a polypropylene-ethylene/propylene copolymer block polymer. The number-average molecular weight ( $M_n$ , in terms of PP) of the resulting polymer was 99,000,  $M_w/M_n$  was 1.06, and the ethylene content was 70.9 % by mol.

In comparison with the polyethylene prepolymer prepared in Example 39, this polymer was increased in the molecular weight with keeping a narrow molecular weight distribution, and ethylene was incorporated into the polymer. From this, it can be seen that a polypropylene-ethylene/propylene diblock copolymer was quantitatively produced. The ethylene content in the second block component (ethylene/propylene copolymer portion), as calculated from the molecular weight and the propylene content in the whole polymer, was 18.4 % by mol.

#### Example 48

In a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of toluene was placed, and propylene was passed through the autoclave at a rate of 100 l/hr to saturate the system. Thereafter, 2.5 mmol (in terms of aluminum atom) of methylaluminoxane and then 0.02 mmol of the titanium compound (1) were added to initiate polymerization at room temperature (24°C). After the polymerization was conducted for 5 hours, feeding of propylene was stopped, and feeding of ethylene at a rate of 1.5 l/hr was started. After the polymerization was conducted at room temperature for 40 minutes, a small amount of isobutanol was added to terminate the polymerization. The whole amount of the resulting

polymer slurry was introduced into 1.5 liters of methanol, and a small amount of hydrochloric acid was added. Then, the mixture was filtered to collect a polymer. The polymer was washed with methanol and then vacuum dried at 80°C for 10 hours. The yield of the polymer after drying was 2.53 g. As a result of GPC measurement, the number-average molecular weight of the polymer was 160,300, and Mw/Mn was 1.51.

Of the whole amount of the resulting polymer, 50 mg of the polymer was dissolved in 0.5 ml of a mixed solvent of orthodichlorobenzene/deutero benzene (mixing ratio: 8/1 by volume) at 110°C, and the following measurements were made in the proton decoupling mode under the following conditions using a JEOL LA500 type nuclear magnetic resonance device.

Pulse angle: 45°, Pulse repetition: 5.5 sec,  
Spectral width: 22000 Hz, Number of scans: 16000,  
Temperature: 120°C, Data points: 32 K

As a result,  $[M^1]$  was 59.7 % by mol,  $[M^2]$  was 40.3 % by mol,  $[M^1 \cdot M^2]$  was 43.4 % by mol,  $[M^1 \cdot M^1]$  was 38.1 % by mol,  $[M^2 \cdot M^2]$  was 18.6 % by mol, the value of  $[M^1 \cdot M^2] / (2 \times [M^1] \times [M^2])$  was 0.90, and the value of  $[M^1 \cdot M^2]^2 / (4 \times [M^1 \cdot M^1] \times [M^2 \cdot M^2])$  was 0.66, with the proviso that the monomer unit  $M^1$  is ethylene, and the monomer unit  $M^2$  is propylene.

The distribution of  $n$  of continuous  $n$  methylenes is as follows.

- [ $n=1$ ]: 37.87 % by mol  
[ $n=2$ ]: 14.59 % by mol  
5 [  $n=3$ ]: 9.96 % by mol  
[ $n=4$ ]: 6.94 % by mol  
[ $n=5$ ]: 7.41 % by mol  
[ $n\geq 6$ ]: 23.23 % by mol

- Methylenes of  $n=3$ ,  $n=5$  and  $n\geq 6$  mean that an isolated  
10 monomer unit  $M^1$  is detected, two continuous monomer units  $M^1$  are detected, and three or more continuous monomer units  $M^1$  are detected, respectively.

Example 49

- 15 In a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of dry toluene was placed, and propylene was passed through the autoclave for 20 minutes at a rate of 100 l/hr. Then, the polymerization temperature was maintained at 25°C, and 5.00 mmol (in terms of aluminum)  
20 of methylaluminoxane was added. Subsequently, 0.05 mmol of the titanium compound (1) was added, and a mixed gas of ethylene and propylene (ethylene: 35 l/hr, propylene: 65 l/hr) was passed through, followed by stirring for 3 minutes and 20 seconds. Then, 20 ml of isobutyl alcohol  
25 was added to terminate the reaction. Subsequently, 10 ml

of a 1N hydrochloric acid aqueous solution was added, followed by stirring for 30 minutes in a stream of nitrogen. The polymer solution was poured into 1.5 liters of methanol to precipitate a polymer, followed by

5 stirring for one night by a magnetic stirrer. The polymer was filtered over a glass filter and dried at 80°C for 10 hours under reduced pressure to obtain 1.19 g of an ethylene/propylene copolymer. As a result of GPC analysis, Mn was 25,100, and Mw/Mn was 1.07. As a result

10 of IR analysis, the propylene content was 24.4 % by mol.

#### Example 50

In a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of dry toluene was placed, and propylene

15 was passed through the autoclave for 20 minutes at a rate of 100 l/hr. Then, the polymerization temperature was maintained at 25°C, and 5.00 mmol (in terms of aluminum) of methylaluminoxane was added. Subsequently, 0.05 mmol of the titanium compound (1) was added, and a mixed gas

20 of ethylene and propylene (ethylene: 35 l/hr, propylene: 65 l/hr) was passed through, followed by stirring for 3 minutes and 20 seconds. Then, a mixed gas of ethylene and propylene having different composition (ethylene: 60 l/hr, propylene: 40 l/hr) was passed through, followed by

25 stirring for 1 minute and 50 seconds. Thereafter, 20 ml

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of isobutyl alcohol was added to terminate the reaction. Subsequently, 10 ml of a 1N hydrochloric acid aqueous solution was added, followed by stirring for 30 minutes in a stream of nitrogen. The polymer solution was poured  
5 into 1.5 liters of methanol to precipitate a polymer, followed by stirring for one night by a magnetic stirrer. The polymer was filtered over a glass filter and dried at 80°C for 10 hours under reduced pressure to obtain 2.29 g of an A-B diblock copolymer. As a result of GPC analysis,  
10 the number-average molecular weight was 40,600, and Mw/Mn was 1.09. As a result of IR analysis, the propylene content was 23.1 % by mol.

#### Example 51

15 In a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of dry toluene was placed, and propylene was passed through the autoclave for 20 minutes at a rate of 100 l/hr. Then, the polymerization temperature was maintained at 25°C, and 5.00 mmol (in terms of aluminum)  
20 of methylaluminoxane was added. Subsequently, 0.05 mmol of the titanium compound (1) was added, and a mixed gas of ethylene and propylene (ethylene: 35 l/hr, propylene: 65 l/hr) was passed through, followed by stirring for 3 minutes and 20 seconds. Then, a mixed gas of ethylene  
25 and propylene having different composition (ethylene: 60



1/hr, propylene: 40 l/hr) was passed through, followed by stirring for 1 minute and 50 seconds. Then, an ethylene gas was passed through at a rate of 100 l/hr, followed by stirring for 1 minute and 10 seconds. Thereafter, 20 ml  
5 of isobutyl alcohol was added to terminate the reaction. Subsequently, 10 ml of a 1N hydrochloric acid aqueous solution was added, followed by stirring for 30 minutes in a stream of nitrogen. The polymer solution was poured into 1.5 liters of methanol to precipitate a polymer,  
10 followed by stirring for one night by a magnetic stirrer. The polymer was filtered over a glass filter and dried at 80°C for 10 hours under reduced pressure to obtain 3.79 g of an A-B-C triblock copolymer. As a result of GPC analysis, the number-average molecular weight was 59,000,  
15 and Mw/Mn was 1.11. As a result of IR analysis, the propylene content was 19.5 % by mol.

#### Example 52

In a 500 ml glass autoclave thoroughly purged with  
20 nitrogen, 250 ml of toluene was placed, and ethylene was fed to saturate the liquid phase and the gas phase. Thereafter, 1.25 mmol (in terms of aluminum atom) of methylaluminoxane and then 0.0002 mmol of the titanium compound (2) were added to initiate polymerization.  
25 After the reaction was conducted at 50°C for 2 minutes in

an ethylene gas atmosphere at ordinary pressure, a small amount of methanol was added to terminate the polymerization. After the polymerization was completed, to the reaction product were added a small amount of

5 hydrochloric acid and a large amount of methanol to precipitate the whole polymer, followed by filtration. The polymer was vacuum dried at 80°C for 10 hours to obtain 0.213 g of polyethylene (PE). The polymerization activity was 3.20 kg based on 1 mmol of titanium. The

10 number-average molecular weight ( $M_n$ ) and the weight-average molecular weight ( $M_w$ ) of the resulting PE were 73,300 and 79,900, respectively, and  $M_w/M_n$  was 1.08.

#### Example 53

15 In a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of toluene was placed, and ethylene (100 l/hr) and hydrogen (5 l/hr) were blown into the autoclave for 10 minutes with stirring. Thereafter, 1.25 mmol (in terms of aluminum atom) of methylaluminoxane and then

20 0.0002 mmol of the titanium compound (2) were added to initiate polymerization. After the reaction was conducted at 50°C for 2 minutes with blowing ethylene and hydrogen into the autoclave, a small amount of methanol was added to terminate the polymerization. After the

25 polymerization was completed, to the reaction product

were added a small amount of hydrochloric acid and a large amount of methanol to precipitate the whole polymer, followed by filtration. The polymer was vacuum dried at 80°C for 10 hours to obtain 0.195 g of polyethylene (PE).

- 5 The polymerization activity was 2.93 kg based on 1 mmol of titanium. The number-average molecular weight (Mn) and the weight-average molecular weight (Mw) of the resulting PE were 59,500 and 69,700, respectively, and Mw/Mn was 1.17.

10

Examples 54 - 58

- Polymerization was conducted in the same manner as in Example 53, except that the catalytic amount, the feed rate of hydrogen and the polymerization time were changed as shown in Table 3. The polymerization activity, molecular weight of the resulting polymer and molecular weight distribution are set forth in Table 3. With increase of the amount of hydrogen, the molecular weight of the resulting polymer was decreased, and even when the polymerization time was prolonged, the molecular weight of the resulting polymer was hardly increased. From this, it can be seen that hydrogen functioned as a chain transfer agent. Even when the polymerization time was prolonged, the polymerization activity was not lowered.
- 15
- 20
- 25 From this, it can be seen that polymerization was further

promoted by the active species produced by the chain transfer reaction.

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Table 3

| Example | Titanium compound<br>Amount<br>(mmol) |       | Amount of<br>MAO<br>(mmol) | Temp<br>(°C) | Time<br>(min.) | Monomer  | H <sub>2</sub><br>(L/h) | Yield<br>(g) | Activity<br>(kg/mmol-Ti·h) | Mn<br>(×10 <sup>4</sup> ) | Mw<br>(×10 <sup>4</sup> ) | Mw/Mn |
|---------|---------------------------------------|-------|----------------------------|--------------|----------------|----------|-------------------------|--------------|----------------------------|---------------------------|---------------------------|-------|
| 53      | 2                                     | 0.002 | 1.25                       | 50           | 2              | Ethylene | None                    | 0.213        | 3.20                       | 7.37                      | 7.99                      | 1.08  |
| 54      | 2                                     | 0.002 | 1.25                       | 50           | 2              | Ethylene | 5                       | 0.195        | 2.93                       | 5.95                      | 6.97                      | 1.17  |
| 55      | 2                                     | 0.002 | 1.25                       | 50           | 2              | Ethylene | 10                      | 0.180        | 2.70                       | 4.28                      | 5.59                      | 1.31  |
| 56      | 2                                     | 0.002 | 1.25                       | 50           | 2              | Ethylene | 20                      | 0.170        | 2.55                       | 2.82                      | 4.27                      | 1.52  |
| 57      | 2                                     | 0.001 | 1.25                       | 50           | 5              | Ethylene | 20                      | 0.203        | 2.44                       | 3.55                      | 5.78                      | 1.63  |
| 58      | 2                                     | 0.001 | 1.25                       | 50           | 15             | Ethylene | 20                      | 0.612        | 2.45                       | 3.93                      | 6.69                      | 1.70  |

Example 59

In a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of toluene was placed, and ethylene was fed to saturate the liquid phase and the gas phase.

- 5 Thereafter, 1.25 mmol (in terms of aluminum atom) of methylaluminoxane, 0.08 mmol of diethylzinc and then 0.002 mmol of the titanium compound (2) were added to initiate polymerization. After the reaction was conducted at 50°C for 2 minutes in an ethylene gas
- 10 atmosphere at ordinary pressure, a small amount of methanol was added to terminate the polymerization. After the polymerization was completed, to the reaction product were added a small amount of hydrochloric acid and a large amount of methanol to precipitate the whole
- 15 polymer, followed by filtration. The polymer was vacuum dried at 80°C for 10 hours to obtain 0.209 g of polyethylene (PE). The polymerization activity was 3.14 kg based on 1 mmol of titanium. The number-average molecular weight (Mn) and the weight-average molecular
- 20 weight (Mw) of the resulting PE were 51,500 and 70,300, respectively, and Mw/Mn was 1.37.

Examples 60 - 62

- 25 Polymerization was conducted in the same manner as in Example 59, except that the amount of diethylzinc and

the polymerization time were changed as shown in Table 4. The polymerization activity, molecular weight of the resulting polymer and molecular weight distribution are set forth in Table 4.

- 5        With increase of the amount of the zinc compound, the molecular weight of the resulting polymer was decreased, and even when the polymerization time was prolonged, the molecular weight of the resulting polymer was hardly increased. From this, it can be seen that the
- 10   zinc compound functioned as a chain transfer agent. Even when the polymerization time was prolonged, the polymerization activity was not lowered. From this, it can be seen that polymerization was further promoted by the active species produced by the chain transfer
- 15   reaction.

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Table 4

| Example | Titanium Compound<br>Amount<br>(mmol) | Amount of<br>MAO<br>(mmol) | Temp<br>(°C) | Time<br>(min.) | Monomer  | Et <sub>2</sub> Zn<br>(mmol) | Yield<br>(g) | Activity<br>(kg/mmol·M·h) | Mn<br>(×10 <sup>4</sup> ) | Mw<br>(×10 <sup>4</sup> ) | Mw/Mn |
|---------|---------------------------------------|----------------------------|--------------|----------------|----------|------------------------------|--------------|---------------------------|---------------------------|---------------------------|-------|
| 59      | (2)                                   | 0.002                      | 50           | 2              | Ethylene | 0.08                         | 0.209        | 3.14                      | 5.15                      | 7.03                      | 1.37  |
| 60      | (2)                                   | 0.002                      | 50           | 2              | Ethylene | 0.16                         | 0.209        | 3.14                      | 4.18                      | 6.06                      | 1.45  |
| 61      | (2)                                   | 0.002                      | 50           | 5              | Ethylene | 0.16                         | 0.511        | 3.07                      | 8.17                      | 12.6                      | 1.54  |
| 62      | (2)                                   | 0.002                      | 50           | 15             | Ethylene | 0.16                         | 1.324        | 2.65                      | 11.2                      | 19.0                      | 1.69  |



Example 63

In a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of toluene was placed, and ethylene was fed to saturate the liquid phase and the gas phase.

- 5    Thereafter, 1.25 mmol (in terms of aluminum atom) of methylaluminoxane and then 0.002 mmol of the titanium compound (3) were added to initiate polymerization. After the reaction was conducted at 50°C for 10 minutes in an ethylene gas atmosphere at ordinary pressure, a
- 10   small amount of methanol was added to terminate the polymerization. After the polymerization was completed, to the reaction product were added a small amount of hydrochloric acid and a large amount of methanol to precipitate a polymer. The polymer was filtered, washed
- 15   with methanol and vacuum dried at 80°C for 10 hours to obtain 0.247 g of polyethylene (PE). The polymerization activity was 0.74 kg based on 1 mmol of titanium. The number-average molecular weight ( $M_n$ ) and the weight-average molecular weight ( $M_w$ ) of the resulting PE were
- 20   88,500 and 98,800, respectively, and  $M_w/M_n$  was 1.12.

Example 64

- Polymerization was conducted in the same manner as in Example 63, except that the amount of the titanium
- 25   compound (3) was changed to 0.001 mmol and the

polymerization time was changed to 15 minutes. Thus, 0.161 g of polyethylene (PE) was obtained. The polymerization activity was 0.64 kg based on 1 mmol of titanium. The number-average molecular weight ( $M_n$ ) and the weight-average molecular weight ( $M_w$ ) of the resulting PE were 145,000 and 167,000, respectively, and  $M_w/M_n$  was 1.15.

#### Comparative Example 1

- 10 In a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of toluene was placed, and ethylene was fed to saturate the liquid phase and the gas phase. Thereafter, 1.25 mmol (in terms of aluminum atom) of methylaluminumoxane and then 0.0005 mmol of zirconocene
- 15 dichloride were added to initiate polymerization. After the reaction was conducted at 25°C for 0.5 minute in an ethylene gas atmosphere at ordinary pressure, a small amount of methanol was added to terminate the polymerization. After the polymerization was completed,
- 20 to the reaction product were added a small amount of hydrochloric acid and a large amount of methanol to precipitate the whole polymer, followed by filtration over a glass filter. The polymer was vacuum dried at 80°C for 10 hours to obtain 0.229 g of polyethylene (PE).
- 25 The polymerization activity was 55.0 kg based on 1 mmol

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of zirconium. The number-average molecular weight ( $M_n$ ) of the resulting PE was 114,000, and  $M_w/M_n$  was 1.99.

#### Comparative Example 2

- 5 Polymerization was conducted in the same manner as in Comparative Example 1, except that the polymerization time was changed to 1 minute. Thus, 0.433 g of polyethylene (PE) was obtained. The polymerization activity was 52.0 kg based on 1 mmol of zirconium. The
- 10 number-average molecular weight ( $M_n$ ) of the resulting PE was 136,000, and  $M_w/M_n$  was 2.26.

#### Comparative Example 3

- 15 Polymerization was conducted in the same manner as in Comparative Example 1, except that 0.00025 mmol of the titanium compound (9) was used instead of the zirconium compound and the polymerization time was changed to 1 minute. Thus, 0.253 g of polyethylene (PE) was obtained. The polymerization activity was 60.7 kg based on 1 mmol
- 20 of titanium. The number-average molecular weight ( $M_n$ ) and the weight-average molecular weight ( $M_w$ ) of the resulting PE were 184,000 and 370,000, respectively, and  $M_w/M_n$  was 2.01.

- 25 Comparative Example 4

Polymerization was conducted in the same manner as in Comparative Example 1, except that 0.0005 mmol of the titanium compound (10) was used instead of the zirconium compound and the polymerization time was changed to 1  
5 minute. Thus, 0.267 g of polyethylene (PE) was obtained. The polymerization activity was 32.0 kg based on 1 mmol of titanium. The number-average molecular weight ( $M_n$ ) and the weight-average molecular weight ( $M_w$ ) of the resulting PE were 129,000 and 229,000, respectively, and  
10  $M_w/M_n$  was 1.78.

#### Comparative Example 5

In a 100 ml reactor thoroughly purged with nitrogen, 50 ml of toluene was placed. The system was cooled to  
15 0°C, and ethylene was fed to saturate the liquid phase and the gas phase. Thereafter, 0.0125 mmol of dimethylaniliniumtetrakis(pentafluorophenyl)borate and then 0.0125 mmol of the hafnium compound (11) were added to initiate polymerization. After the reaction was  
20 conducted at 0°C for 1 minute in an ethylene atmosphere at ordinary pressure, a small amount of methanol was added to terminate the polymerization. The reaction product was introduced into a large amount of methanol to precipitate a polymer. The polymer was filtered, then  
25 washed with methanol and vacuum dried at 80°C for 10

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hours to obtain 0.290 g of polyethylene (PE). The number-average molecular weight (Mn) of the resulting PE was 132,400, and Mw/Mn was 1.85.

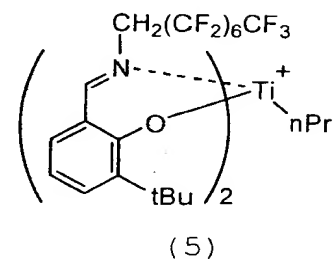
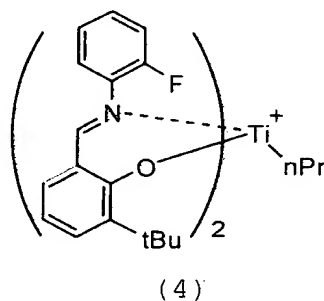
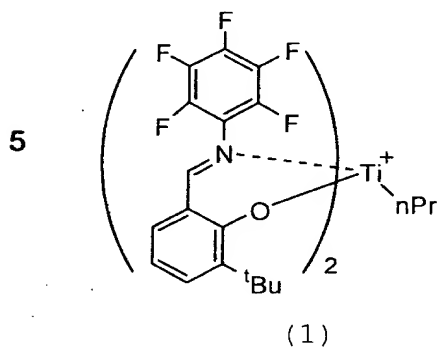
5 Comparative Example 6

Polymerization was conducted in the same manner as in Comparative Example 5, except that the amount of the hafnium compound (11) and the amount of the dimethylaniliniumtetrakis(pentafluorophenyl)borate were each changed to 0.005 mmol and the polymerization temperature was changed to 50°C. Thus, 0.148 g of polyethylene (PE) was obtained. The number-average molecular weight (Mn) of the resulting PE was 98,800, and Mw/Mn was 1.91.

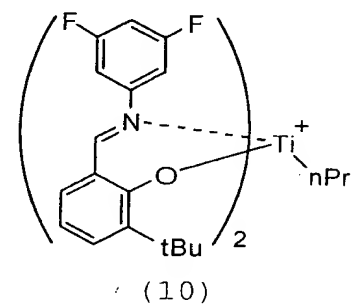
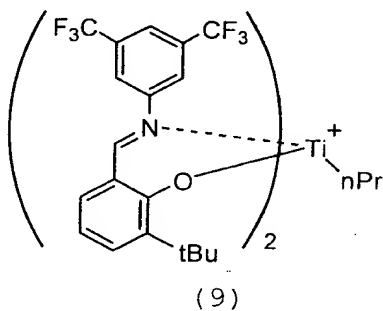
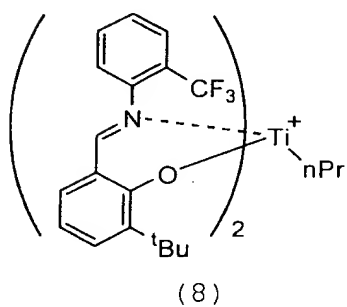
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Calculation examples of complex structure parameters



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$H^{\beta}$ -Z Distance ( $r(H^{\beta}-Z)$ ) and electrostatic interaction energy ( $ES_p(H^{\beta}-Z)$ ) of each catalyst

| Compound                        | (1)   | (4)   | (5)   | (8)   | (9)   | (10)  |
|---------------------------------|-------|-------|-------|-------|-------|-------|
| $r(H^{\beta}-Z)$ (Å)            | 2.275 | 2.329 | 2.234 | 2.498 | 2.246 | 4.812 |
| $ES_p(H^{\beta}-Z)$<br>(KJ/mol) | -37.1 | -41.1 | -42.9 | -33.1 | -12.0 | -10.2 |